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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 71 Number 1

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THE SOCIETY OF DYERS AND COLOURISTS
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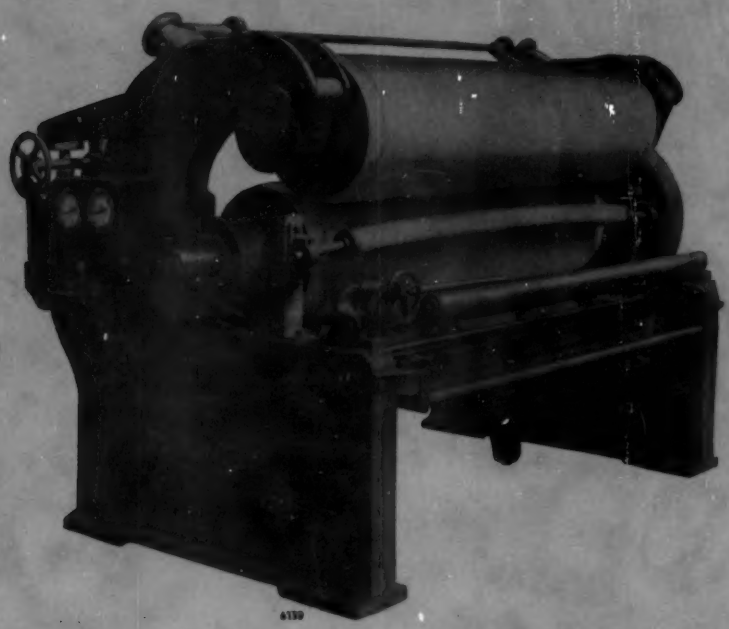

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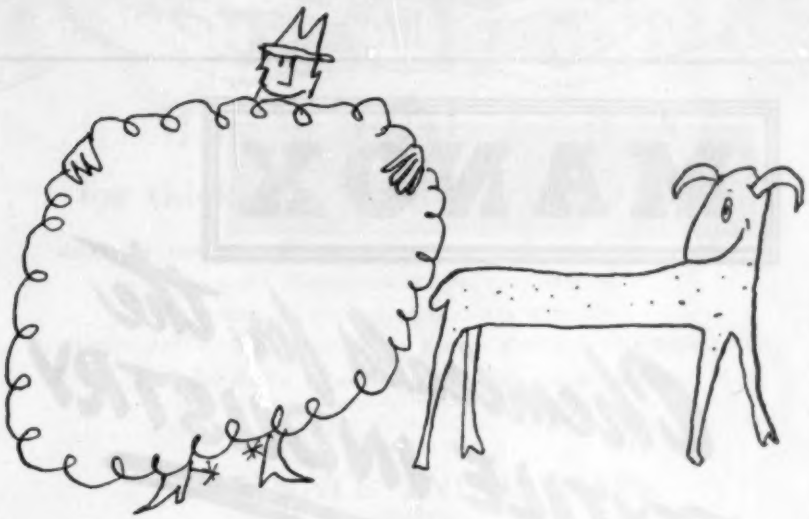

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1955 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Behaviour of Leuco Vat Dyes at Temperatures greater than 100°C.
S. Blackburn and M. R. Fox

The Preparation, Use, and Evaluation of Metallic Pigments *G. W. Wendon*

COMMUNICATIONS

The Influence of the Physical State of Dyes upon their Light Fastness
G. Baxter, C. H. Giles, Miss M. N. McKee, and N. Macaulay

The Polarography of Azo Dyes *J. de O. Cabral and H. A. Turner*

The Mechanisms of Some Reactions between *N*-Halogenoamines and Wool *C. Earland*

The Dyeing of Acetate Rayon with Disperse Dyes
III—The Influence of Dispersing Agents on Rate of Dyeing
Miss P. Harris, F. Manchester, and C. L. Bird

The Affinities of Vat Dyes in relation to their Constitution *R. H. Peters and H. H. Sumner*

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ANNUAL DINNER

on 1st April 1955

at the Queens Hotel Leeds

As accommodation at the Queens Hotel is now **fully booked** for the above function, intending visitors are advised to contact the Hotel Metropole (*Telephone* Leeds 20841) which is nearest to the Queens Hotel, or the Great Northern Hotel (*Telephone* Leeds 30431).

Advance ticket reservations are invited by letter addressed to the Society.

FORTHCOMING MEETINGS OF THE SOCIETY

Tuesday, 25th January 1955

LEEDS JUNIOR BRANCH. *Some Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., F.R.I.C., A.T.I. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 26th January 1955

MIDLANDS SECTION. *I do it this way!* Demonstrations of novel testing techniques by local members. College of Technology, **Leicester.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Processing of "Dynel" Textiles.* D. H. Stott, Esq. (Gemec Chemical Company). **Bradford** Technical College. 7.15 p.m.

Thursday, 27th January 1955

WEST RIDING SECTION. *Some Aspects of Anthraquinone Dyestuffs Chemistry.* Dr. S. Coffey (Imperial Chemical Industries Ltd.). The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Friday, 28th January 1955

LONDON SECTION. Annual Dinner Dance at The Waldorf Hotel, **London W.C.2.**

Tuesday, 1st February 1955

MANCHESTER JUNIOR BRANCH. *Rates of Uptake of Vat Dyes by Cellulose.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th February 1955

LONDON SECTION. *Textile Performance Standards for the Distributor.* Messrs. F. Cowles and J. S. Ingham (Marks and Spencer Ltd.). Royal Society Rooms, Burlington House, **London W.1.** 6 p.m.

Tuesday, 8th February 1955

MANCHESTER SECTION. Joint meeting with the Textile Institute in Macclesfield. *The Dyeing Properties of "Terylene" Polyester Fibre.* J. G. Graham, Esq., B.Sc. Fuller details later.

LEEDS JUNIOR BRANCH. *The Printing of Wool including the Production of Melange Effects.* J. A. Potter, Esq., M.A., F.S.D.C. (Messrs. Clayton Dyestuffs Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

Wednesday, 9th February 1955

NORTHERN IRELAND SECTION. *Fastnesses of Coloured Textiles as they Affect the General Public.* J. S. Ingham Esq. (Marks & Spencer Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th February 1955

WEST RIDING SECTION. Details Later.

Tuesday, 15th February 1955

HUDDERSFIELD SECTION. *Non-Textile Uses of Dyestuffs.* J. P. Gill, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Joint meeting with Huddersfield Section of the Royal Institute of Chemistry. The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *pH in the Textile Industry.* T. Green, Esq., A.M.C.T. (Clayton Dyestuffs Co. Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 18th February 1955

MANCHESTER SECTION. *The Soiling of Synthetic and Natural Fibres.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). Textile Institute. 6.30 p.m.

Monday, 21st February 1955

BRADFORD JUNIOR BRANCH. Messrs. I.C.I. Ltd. and Petroleum Film Bureau. Film Evening.

Wednesday, 23rd February 1955

MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

Thursday, 24th February 1955

WEST RIDING SECTION. *Heat Sensitivity of Anthraquinone Acid Wool Dyes.* Dr. R. H. Peters and Dr. T. Watson (Messrs. I.C.I. Ltd.). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 25th February 1955

MANCHESTER SECTION. Annual Dance.

March 1955

LONDON SECTION. The London Lecture. Details later.

Tuesday, 1st March 1955

LEEDS JUNIOR BRANCH. *The Application of Azoic Dyes to "Terylene" Polyester Fibre at 100-130° C.* H. R. Hadfield, Esq., M.Sc. (Messrs. I.C.I. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

MANCHESTER JUNIOR BRANCH. *Synthetic Fibres in the Hosiery Industry.* Member of the staff of Clayton Dyestuffs Co., Manchester. (To be announced later). College of Technology, **Manchester.** 6.30 p.m.

Friday, 4th March 1955

MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955

NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955

MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

WEST RIDING SECTION. Title Later. Dr. F. F. Elsworth (Wool Industries Research Association). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 15th March 1955

HUDDERSFIELD SECTION. *Sulphur Colours for Special Purposes.* H. Senior, Esq. (James Robinson & Co. Ltd.). Preceded by Annual General Meeting, Princess Cafe, **Huddersfield.**

LEEDS JUNIOR BRANCH. *The Classification of Dyes by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. (The Geigy Co. Ltd.). Departmental Lecture Theatre, The University, **Leeds.** 3.30 p.m.

SCOTTISH SECTION — LADIES' EVENING. *The Hand Printing of Textiles.* E. S. Beton, Esq. (Brocklehurst, Whiston Amalgamated Ltd.). Institution of Engineers & Shipbuilders, **Glasgow.** 7 p.m.

Thursday, 17th March 1955

BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Acetate Woven and Knitted Fabrics.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 18th March 1955

MANCHESTER SECTION. One Day Symposium. Full details later.

Thursday, 24th March 1955

WEST RIDING SECTION—ANNUAL GENERAL MEETING. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 5th April 1955

SCOTTISH SECTION — ANNUAL GENERAL MEETING. 7 p.m. *Primitive and Modern Dyeing Practice.* (Illustrated) (I.C.I. Ltd.). St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 6th April 1955

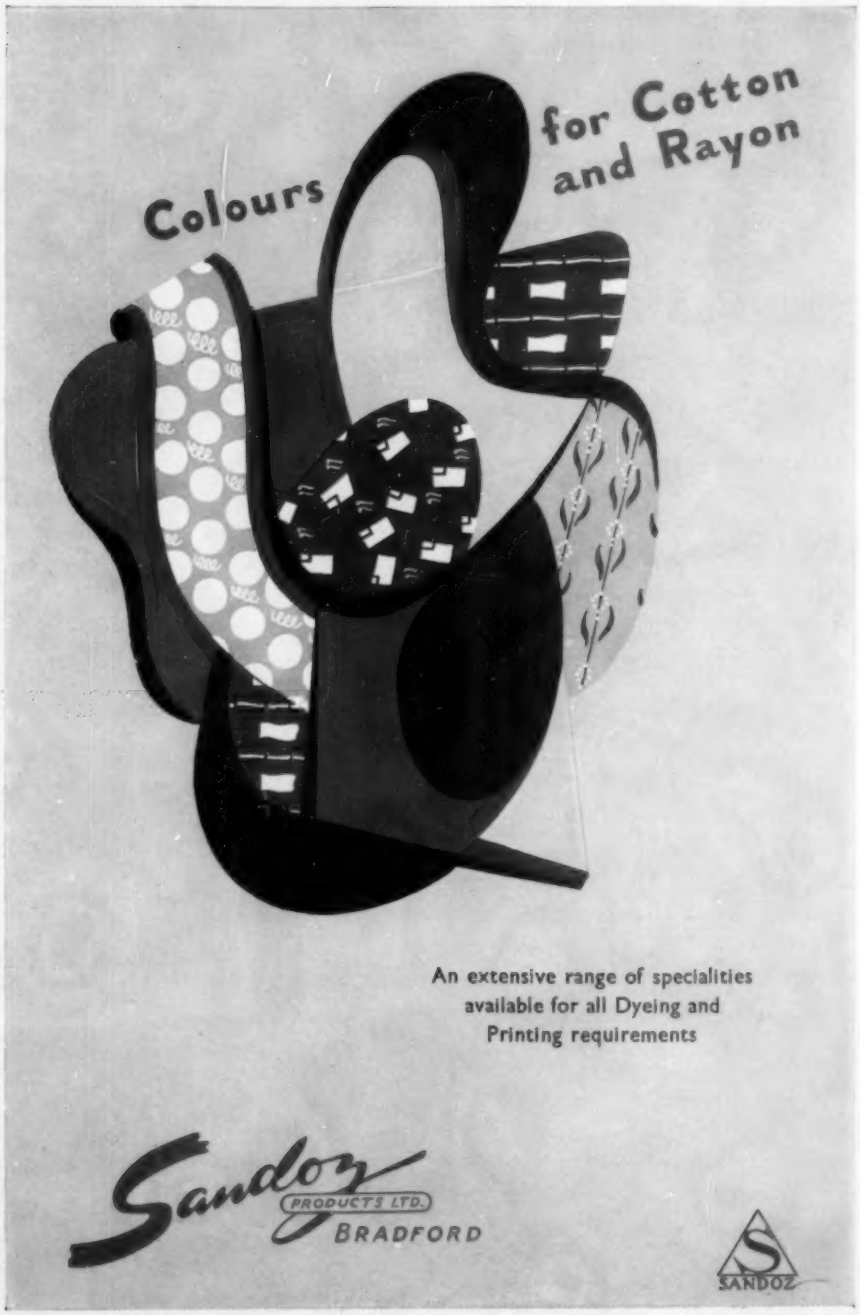
MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Friday, 15th April 1955

MANCHESTER SECTION — ANNUAL GENERAL MEETING. *"Courpleta" The Dyeing and Other Properties of Tiacetate Yarn and Staple.* J. Boulton, Esq., M.Sc. Tech., F.S.D.C., F.T.I. Textile Institute, **Manchester.** 7 p.m.

Thursday, 21st April 1955

MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen. Mill Street, **Kidderminster.** 7 p.m.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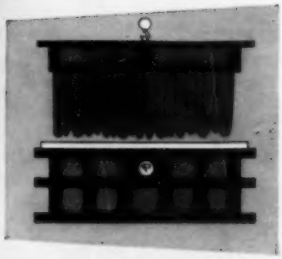

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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 71 Number 1 JANUARY 1955 *Issued Monthly*

OFFICIAL NOTICES

OBJECTS OF THE SOCIETY OF DYERS AND COLOURISTS

To promote the advancement of science and technology, especially in the theory and practice of the tinctorial arts.

To provide means for the wider dissemination and interchange of knowledge concerning the science and technology of colour and colouring matters, of their methods of application, and of the materials to which they may be applied.

To encourage education and research in any or all of the above subjects.

And for the furtherance of these objects—

To hold meetings for the reading of papers, for lectures, and for discussions.

To publish a *Journal*.

And to do all such other things as may be conducive to the attainment of these objects.

ELECTION OF OFFICERS AND MEMBERS OF COUNCIL

Under the revised Bye-laws which are now operative, Officers and Members of Council—other than the President and President-elect, who are nominated by Council and elected at the Annual General Meeting—are to be elected by a Postal Ballot of the members.

The attention of members is drawn to Bye-laws No. 12–21 inclusive and 22–26 inclusive, which relate to Officers and Members of Council respectively.

Nominations to be valid must be received by the Honorary Secretary of the Society at least six weeks prior to the date of the Annual General Meeting, which is on 1st April 1955.

MEMBERS AND JUNIOR MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the Secretary or from the Honorary Secretary of any Section of the Society. Applications must be proposed and seconded by members to whom the applicants are known personally. The rates of annual subscription are as follows—

(i) During the period of "full-time national service" the annual subscription to be waived entirely. Such members will be asked whether they wish to receive the *Journal*.

(ii) Ordinary Members between the ages of 21 and 25 years who are students, i.e. who are pursuing an accepted course, full or part time, at a recognised technical college or university and vouched for by the head of their department or other responsible person—15s. 0d.

(iii) Other Ordinary Members between the ages of 21 and 25 years—£2 2s. 0d.

(iv) Members having had forty years' continuous membership of the Society to be given the option of paying half the current annual subscription (vi) for Ordinary Members.

(v) Members having had fifty years' continuous membership of the Society—the annual subscription to be waived entirely.

(vi) All other Ordinary Members—£3 3s. 0d.

(vii) All other Junior Members—15s. 0d.

FELLOWS, ASSOCIATES, AND REGISTERED STUDENTS

The Society confers diplomas in tinctorial technology on suitably qualified members. These distinctions are in two grades—the Associateship and the Fellowship—and confer the right to use the title Associate of the Society of Dyers and Colourists (A.S.D.C.) or Fellow of the Society of Dyers and Colourists (F.S.D.C.). To obtain the Associateship candidates are required to pass the prescribed examinations and to furnish evidence of satisfactory general education and of training and experience in at least one branch of the manufacture or application of colouring matters. The Fellowship is conferred on senior members who have attained high standing in the knowledge and practice of tinctorial technology. Students who intend to take the Society's examination are strongly recommended to become Registered Students, so that their studies and preparation may be effectively directed.

Copies of the regulations and syllabuses may be obtained on application to The Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire.

The *JOURNAL*

The *Journal* is posted free to all Members. Non-members can obtain copies on application to the Offices of the Society. All orders must be accompanied by a remittance of 6s. 8d. per copy (£4 0s. 0d. per annum post free). Back numbers of most issues of the Society's *Journal* can be supplied.

Members are reminded that under Bye-law 41 the *Journal* will not be forwarded to those who have not paid their subscription by 30th June 1955.

Members residing abroad are particularly requested to inform the Secretary by separate post when sending their subscriptions by Money Order.

Communications on any subject related to the objects of the Society, especially such as are of an original character, are invited for consideration for publication in the *Journal*. Such Communications in the first instance should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire.

The *JOURNAL*—*contd.*

General communications, including inquiries or orders for advertisements, should be addressed to the Offices of the Society, to which address all remittances should be sent.

REPRINTS OF LECTURES AND COMMUNICATIONS

Reprints of all lectures and communications are available after publication to members of the Society and non-members. The charges (postage included) are as follows— Single copies 2s. 6d. each; per dozen copies up to and including 8 pages, 12s. 6d., and for papers occupying more than 8 pages of the *Journal*, 17s. Orders should be addressed to "The Society of Dyers and Colourists, 19 Piccadilly, Bradford 1". They can be accepted only if accompanied by remittance and if received immediately after publication of the paper.

ABSTRACTS SECTION

Attention is drawn to the fact that copies of the Abstracts Section of the *Journal* printed on only one side of the paper, so that individual abstracts can be cut out and pasted on cards, are available at a charge of 30s. 0d. per annum. Orders should be sent to the Society's offices at 19 Piccadilly, Bradford 1, Yorkshire.

FREE ADVERTISEMENTS

For the convenience of members the Publications Committee allows a limited number of advertisements relating to SITUATIONS WANTED to be inserted in the *Journal gratis*. Such advertisements must not exceed 24 words in length.

Replies may be addressed, *Box—, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire.*

NOTICE TO AUTHORS OF PAPERS

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. Centre headings should be employed sparingly. Side headings should be indented and underlined, and run into the text to which they apply by means of a dash. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and they should be indicated by small circles rather than by crosses in the case of a single graph, but where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

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Many of the books and periodicals reviewed or abstracted in the *Journal* since 1948 (and in some cases earlier) are retained by the Society, and may be borrowed by members. Enquiries and applications should be directed to the Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire.

LIBRARY OF THE CHEMICAL SOCIETY—LOAN OF BOOKS

Members of the Society may borrow books from the very extensive collection of works on pure and applied chemistry in the Library of the Chemical Society, by applying direct to *The Librarian, Chemical Society, Burlington House, Piccadilly, London W.1* (*REGent 0675–6*), *and referring to their membership of the Society of Dyers and Colourists.* Letters on the subject should *not* be addressed to the Offices of the Society in Bradford.

DEPOSIT OF SEALED COMMUNICATIONS

I— The Society is prepared to receive from members and others and to keep as deposits, Sealed Communications dealing with any subject relating to the theory or practice of the Dyeing, Printing, and kindred industries.

II— Every deposit must bear on the cover a title for classification, the author's name, the date, and must be secured by a distinctive seal.

III— The deposit should be written in English, and, if it deals with machinery, be accompanied by sketches or drawings, or, in the case of dyeing or printing processes, by patterns.

IV— Every deposit will, unopened, be signed and sealed by the Honorary Secretary of the Society, immediately after receipt, and countersigned by another member of the Council.

V— The deposits will be numbered and entered into a special register, and an official receipt will be sent to the author.

VI— No charge will be made for registration and deposit.

VII— The deposits will be kept by the Society for a period of seven years. At the end of this period they will be opened and the contents read before the next meeting of the Council of the Society, and the contents, or an abstract thereof, may be published in the *Journal* of the Society at the discretion of the Publications Committee.

VIII— The author shall have the right to recall his deposit unopened at any time within the said seven years, or he may, at any time, order it to be opened and read before one of the Society's meetings. Such instructions must be accompanied by the official receipt.

IX— The Society will take every reasonable care of the deposits, but cannot be held responsible for their loss.

MEDALS AND AWARDS

HONORARY MEMBERS OF THE SOCIETY

1886–1915	*Sir H. E. Roscoe, M.P.
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1908–1915	*Prof. Dr. C. Liebermann
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1927–1930	*Ernest Hickson
1928–1939	*R. E. Schmidt
1931–1933	*Alfred Rée, Ph.D.
1932–1940	*W. M. Gardner
1934–1947	*George Douglas
1934–1946	*H. Grandage
1934–1940	*Christopher Rawson
1941–1948	*Prof. E. C. C. Baly, C.B.E., M.Sc., F.R.S.
1944–1946	*Prof. F. M. Rowe, D.Sc., F.R.I.C., F.R.S.
1946–1946	*James S. Ridsdale
1947	C. J. T. Cronshaw, D.Sc., F.R.I.C., M.I.Chem.E., F.T.I., F.R.S.E., F.S.D.C.
1948	H. Jennison, M.C., A.M.C.T., A.R.I.C., F.S.D.C.
1950–1953	*George E. Holden, C.B.E., M.Sc., F.R.I.C.
1953	John Barritt, B.Sc., A.R.C.S., A.R.I.C., F.S.D.C.

The following have been *ex officio* Honorary Members of the Society, the later dates indicating termination or change in title of the office—

1886–1920	The Worshipful Master of the Dyers' Company
1920–	The Prime Warden of the Worshipful Company of Dyers
1886–1900	The President, Bradford Technical College
1900–1905	*W. E. B. Priestley, Chairman of the Technical Instruction Committee of the Bradford City Council

*Deceased

THE PERKIN MEDAL

The Perkin Medal was modelled by the late F. W. Pomeroy, R.A., for the Society. It is an excellent presentation of the head of Sir William Perkin, the founder of the coal-tar colour industry, and President of the Society in 1907.

This medal is awarded for discoveries or work of outstanding importance in connection with the tinctorial arts.

LIST OF RECIPIENTS

1908	Professors Graebe and Liebermann. "Synthesis of Alizarin."
1911	Prof. Adolf von Baeyer. "Synthesis of Indigo."
1914	Comte Hilaire de Chardonnet. "Artificial Silk."
1917	Prof. Arthur G. Green. "Primuline."
1919	R. Vidal. "Sulphur Black."
1921	Horace Lowe. "Permanent Lustre on Cotton."
1923	Chas. F. Cross. "Discovery of Viscose."
1925	M. Prud'homme. "Aniline Black and Alizarin Blue."
1928	Dr. Robert E. Schmidt. "For Epoch-making Discoveries of Anthraquinone Derivatives and Dyestuffs therefrom."
1938	Dr. H. Dreyfus. "For Discoveries and Work of Outstanding Importance in Connection with the Development of the Cellulose Acetate Rayon Industry in England."
1938	J. Baddiley. "In recognition of his National Services for the Renaissance of the British Dyestuffs Industry through Many Important Investigations in the Field of Colour Chemistry Conducted or Directed by him."
1950	Prof. J. B. Speakman. "In recognition of his Outstanding Contributions to the Science and Technology of Textiles."
1954	Dr. Arthur Zitscher. "For his Work leading to the Discovery of the New Class of Azoic Dyes, based on the Arylamides of *o*-Hydroxycarbóxylic Acids."

THE MEDAL OF THE SOCIETY OF DYERS AND COLOURISTS

This Medal was instituted by the Society in 1908. Of the competitive designs submitted, that of Mr. Edgar Lockwood was selected. The design indicates that the work of the dyer (centre figure) is both a science (right background) and an art (left foreground).

1908–1927 The Medal was occasionally awarded as a recognition of work of exceptional merit carried out under the Society's Research Scheme.

From 1928 The Medal was awarded as a recognition of exceptional services (*a*) to the Society or (*b*) in the interests of the Tinctorial and Allied Industries.

LIST OF RECIPIENTS

1908 J. B. Fothergill (Bronze Medal). "Treatment of Cotton to Cause it to Resist Direct Dyeing Colours."

1912 J. H. Garner (Silver Medal). "Treatment of Effluents from Dyehouses and Textile Factories."

1928 Ernest Hickson (Gold Medal). "Exceptional Services rendered to the Society as Chairman of the Publications Committee 1897–1925, and Chairman of *Colour Index* Committee."

1930 Arthur Silverwood (Gold Medal). "Exceptional Services rendered to the Society as Honorary Secretary 1913–1930."

1933 Prof. Walter M. Gardner (Gold Medal). "Distinguished Services as Editor of the Society's *Journal* 1900 to 1932."

1934 Prof. F. M. Rowe (Gold Medal). "Exceptional Services to the Society and to the Tinctorial Industries as Editor of the *Colour Index* 1924 and the 'Supplement' 1928."

L. A. Lantz (*Chairman*), H. H. Bowen, P. W. Cunliffe, R. S. Horsfall, Prof. B. A. McSwiney, C. C. N. Vass, C. M. Whittaker, S. G. Barker (Silver Medals). "Exceptional Services to the Society as Members of the Standardisation of Fastness Executive Committee."

1936 W. A. Edwards (Silver Medal). "Valuable Services rendered to the Society as Honorary Secretary of the Midlands Section since its inception in 1919 to 1935."

1937 R. Ritchie (Silver Medal). "Devoted and Valuable Services as Honorary Secretary of the Scottish Section for eighteen years."

1940 F. L. Goodall (Gold Medal). "Valuable Services to the Tinctorial Industries by his work on the Theory and Practice of Wool Dyeing."

1943 C. M. Whittaker (Gold Medal). "In recognition of Exceptional Services in promoting Scientific and Technical Knowledge amongst Textile Colourists, and for Sustained and Outstanding Service to the Society."

1946 H. H. Bowen (Gold Medal). "For Outstanding Services to the Society and in recognition of his Chairmanship of the Publications Committee for a period of twenty years."

H. H. Hodgson (Gold Medal). "For Outstanding Services to the Society and for his series of Sustained Experimental and Theoretical Contributions to those chapters of Organic Chemistry which are the essential scientific background to the Dyestuffs Industry."

E. Race (Silver Medal). "For his Valued Services to the Society as Joint Author of thirteen papers published in the Society's *Journal*."

H. Turner (Silver Medal). "In recognition of his Valuable Services to the Society and of his twenty-two years' service as Honorary Secretary of the Huddersfield Section."

Mrs. E. Cummings (*née* Levin) (Silver Medal). "For her Valued Services to the Society; by her assistance rendered in the preparation of the first *Colour Index*; by her Joint Authorship of a number of Papers published in the *Journal* of the Society, and as an Abstractor for the *Journal* of the Society for twenty years."

1947 Fred Smith (Gold Medal). "For Exceptional Services to the Society over a period of thirty-seven years comprising Chairman, West Riding Section; Member of Council and of many important Committees."

F. Scholefield (Gold Medal). "In recognition of Exceptional Services to the Society in the advancement of Tinctorial Technology both in theory and practice."

C. Schardt (Silver Medal). "In recognition of his Valuable Services to the Society over a period of twenty-four years including Chairman, Vice-Chairman, and member, of the Midlands Section Committee."

1948 G. G. Hopkinson (Gold Medal). "For Valuable Services rendered to the Society and to the Dyeing Industry."

D. B. F. McAndrew (Silver Medal). "For Valuable Services rendered to the Society as Honorary Secretary and Committee Member of the Scottish Section 1935–1947."

C. O. Clark (Silver Medal). "For Valuable Services rendered to the Society from 1923 to 1948."

1949 S. M. Neale (Gold Medal). "For his Pioneer Work in the Application of the Methods of Physical Chemistry to the Elucidation of the Phenomena of Dyeing, more particularly of Cellulosic Materials with Substantive Dyes."

1950 P. W. Cunliffe (Gold Medal). "For Outstanding Services to the Society and to the Tinctorial and Allied Industries."

H. Foster (Gold Medal). "For Outstanding Services to the Society."

L. A. Lantz (Bar attached to Silver Medal previously awarded). "For Exceptional Services to the Society and to the Tinctorial and Allied Industries in connection with Fastness Tests."

1951 W. Kilby (Gold Medal). "For Work on the Development of a Molten Metal Process of Continuous Dyeing."

1953 H. A. Turner (Gold Medal). "For his Valuable Researches contributed to the Tinctorial Industries."

A. W. Carpenter (Silver Medal). "For Valuable Services to the Society."

Miss M. Forbes (Bronze Medal). "For Valuable Services to the Society."

H. R. Hadfield (Bronze Medal). "For Valuable Services to the Society."

THE WORSHIPFUL COMPANY OF DYERS RESEARCH MEDAL

The Medal represents the Arms of the Worshipful Company of Dyers of the City of London, which were granted in 1471. The following is a brief description—

Arms— Sable, a chevron engrailed argent, between three bags of madder of the last, corded or.

Crest— On a wreath three sprigs of the graintree erect vert, fructed gules.

Supporters—Two leopards rampant gardant argent, spotted with various colours; fire issuing from their ears and mouth proper, both ducally crowned or.

Motto— Da Gloriam Deo.

1— The Dyers' Company offer annually a Gold Medal called "The Worshipful Company of Dyers Research Medal", the award of which is open to the Authors of papers embodying the results of scientific research or technical investigation connected with the tinctorial arts submitted to the Society of Dyers and Colourists, and published in the *Journal* of such Society during the twelve months ending on the 30th June in the year for which the Medal is granted, and, in the special circumstance provided for by Rule 6, during the twelve months ending on the 30th June in the year previous to that for which the Medal is granted. If a paper shall be published in two or more parts, then for the purpose of the award of the Medal, all the parts together shall be treated as a paper published in the year in which the final part is published.

2— The Medal will not be awarded to the same person on more than one occasion.

3— The Society of Dyers and Colourists shall consider the papers available for the Medal and advise the Company as to the merits thereof, and if, in the judgment of the Society, none of the papers is of sufficient merit, the Society may recommend that the Medal be not awarded.

4— The Dyers' Company will award the Medal either to the Author of the paper which, in all the circumstances, appears to the Company to show the greatest merit, or, in the event of such paper being the work of an Author who has already been awarded the Medal, to the Author of the paper next in order of merit who has not already been awarded the Medal, and may, if the Company so thinks fit, refrain from making any award.

5— In the event of a paper being the work of two or more persons, the Author shall be taken to be that one of them whose work in the opinion of the Society of Dyers and Colourists has most substantially contributed to the merit of the scientific research or technical investigation embodied in such paper.

6— In the event of the Author of a paper of sufficient merit published in the *Journal* of the Society of Dyers and Colourists during any twelve months for which the Medal is awarded being unsuccessful in obtaining the award of the Medal for that period, the Society of Dyers and Colourists may, in their discretion, consider such paper for adjudication with the papers available for the award of the Medal for the next succeeding twelve months.

LIST OF RECIPIENTS

1908	Prof. E. Knecht. "A Means of Estimating the Degree of Mercerisation in Cotton Yarns."
1909	Prof. Arthur G. Green. "The Chemical Technology of Aniline Black."
1910–11	R. L. Taylor. "The Action of Carbon Dioxide and of Air on Bleaching Powder."
1911–12	W. Harrison. "The Electrical Theory of Dyeing."
1912–13	S. H. Higgins. "Observations on the Bleaching of Cotton" and "The Action of Neutral Salts on Bleaching Solutions."
1913–14	W. Johnson (in conjunction with Prof. Arthur G. Green, who had already been awarded the Medal). "The Constitution of Aged and of Bichromate Aniline Blacks."
1914–15	Morris Fort. "The Mechanism of the Acid Dye-bath."
1915–16	James R. Hannay. "The Interaction between Metallic Copper and certain Dyes of the Thiazine, Oxazine and Azine Series."
1916–17	Prof. H. M. Dawson. "The Phenomena of Acid Catalysis and the Theory of Acids."
1917–18	L. G. Radcliffe. "The Sulphonation of Fixed Oils."
1918–19	Chas. F. Cross (Diplomas presented to M. C. Lamb and C. V. Greenwood as co-authors). "Colloidal Tannin Compounds and their Applications."
1919–20	A. E. Everest (Diploma presented to A. J. Hall as co-author). "The Tinctorial Properties of some Anthocyans and certain Related Compounds."
1920–21	Prof. G. T. Morgan. "The Co-ordination Theory of Valency in Relation to Adjective Dyeing."
1921–22	S. Judd Lewis. "On the Fluorescence of Cellulose and its Derivatives."
1922–23	Prof. Arthur G. Green (Bar attached to Medal previously awarded), and K. H. Saunders. "The Ionamines— A New Class of Dyestuffs for Cellulose Acetate Silk."
1923–24	S. Judd Lewis (Bar attached to Medal previously awarded). "The Quantitative Determination of the Fluorescent Power of Cellulose and its Derivatives."
1924–25	Prof. F. M. Rowe (with Diploma to Miss E. Levin, as co-author). "The Identification of Azo Colours on the Fibre and of Azo Pigments in Substance."
1925–26	H. H. Hodgson. "Behaviour of the Sulphides of Sodium in Aqueous and Alcoholic Media", and "The Action of Sulphur on the Monochloranilines."
1926–27	Prof. F. M. Rowe (Bar attached to Medal previously awarded) and Diplomas awarded to collaborators— Miss E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper. "A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic acid, leading to the preparation of Phthalazine, Phthalazone and Phthalimidine Derivatives."
1927–28	No award.
1928–29	F. Scholefield (with diplomas to Miss E. Hibbert and C. K. Patel as co-authors). "The Action of Light on Dyed Colours."
1929–30	H. H. Hodgson (Bar attached to Medal previously awarded). "Colour and Constitution from the Standpoint of Recent Electronic Theory."
1930–31	Prof. F. M. Rowe (Second Bar attached to Medal previously awarded), and Diplomas awarded to S. Ueno and F. H. Jowett as collaborators. "Insoluble Azo Colours on the Fibre and Action of Boiling Caustic Soda thereon."
1931–32	No award.

1932–33 Two awards— W. T. Astbury. "The X-ray Interpretation of Fibre Structure." J. B. Speakman. "The Structure of the Wool Fibre; its Relation to the Dyeing and Finishing Processes of the Wool Textile Trade."

1933–34 No award.

1934–35 H. A. Turner, and Diplomas awarded to G. M. Nabar and F. Scholefield, as co-authors. "The effect of Reduced Vat Dyes upon the Hypochlorite Oxidation of Cellulose."

1935–36 Prof. F. M. Rowe (Third Bar attached to Medal previously awarded), and Diplomas awarded to C. H. Giles, R. L. M. Allen, W. G. Dangerfield, and Glyn Owen, as collaborators. "Decomposition of Azo Dyes by Acids, Caustic Alkalis, and Reducing Agents."

1936–37 J. B. Speakman (Bar attached to Medal previously awarded), and Diplomas awarded to C. S. Whewell and J. L. Stoves, as collaborators. "The Reactivity of the Sulphur Linkage in Animal Fibres."

1937–38 Prof. F. M. Rowe (Fourth Bar attached to Medal previously awarded), and J. B. Speakman (Second Bar attached to Medal previously awarded), and Diplomas awarded to E. Race and T. Vickerstaff, as collaborators. "The Unlevel Dyeing of Wool with Acid and Chrome Dyes. Part I— The Reasons for the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure, and Part II— A Method for Correcting the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure."

1938–39 No award.

1939–40 T. H. Morton, as senior author of the paper on "Application of Vat Dyes to Viscose Rayon", by J. Boulton and T. H. Morton.

1940–41 No award.

1941–42 T. Vickerstaff, as senior author of the paper on "The Dyeing of Cellulose Acetate Rayon with Dispersed Dyes", by T. Vickerstaff and E. Waters.

1942–43 No award.

1943–44 J. Boulton. "The Importance of Dyeing Rate— an Interpretation for the Practical Dyer of Recent Research on Direct Dyeing."

1944–45 No award.

1945–46 No award.

1946–47 H. Phillips, as senior author of the paper on "The Chemical Constitution and Physical Properties of Bisulphited Wool", by E. G. H. Carter, W. R. Middlebrook, and H. Phillips.

1947–48 J. M. Preston. "Some Factors affecting the Dyeing of Viscose" and "Some Aspects of the Drying and Heating of Textiles".

1948–49 H. Lindley, as major contributor to the paper "The Mechanism of Set and Supercontraction in Wool Fibres", by S. Blackburn and H. Lindley.

1949–50 No award.

1950–51 J. Crank. "The Diffusion of Direct Dyes into Cellulose. III— The Present State of the Theory and its Application".

1951–52 H. Hampson. "Advances in the Application of Vat Dyes to Viscose Rayon Cakes".

1952–53 R. H. Peters, as senior author of the paper on "The Reduction Properties of Vat Dyes", by W. J. Marshall and R. H. Peters.

1953–54 R. J. Hannay, as senior author of the papers "A New Method of pH Control in Dyeing and Some Observations on the Metachrome Process", by R. J. Hannay, W. H. Major, and R. Pickin, and "The Use of Hydrolysable Esters in the Control of Dyebaths", by R. J. Hannay and W. H. Major.

THE WORSHIPFUL COMPANY OF FELTMAKERS RESEARCH MEDAL

The Feltmakers' Company offer annually a Gold Medal for Papers embodying the results of scientific research or technical investigation connected with the art of feltmaking and published in the *Journal* of the Society. Further, in order to encourage research of a type likely to qualify for the award of the Medal, the Feltmakers' Company offer annually, for an initial period of five years, a Research Grant of £50.

1945–1954 No award.

KNECHT MEMORIAL FUND

A Fund of £100 was subscribed as a Memorial to the late Professor Edmund Knecht, from the interest on which two prizes, in the form of books, are awarded annually to selected students of the Manchester College of Technology and the Royal Technical College, Salford.

MERCER LECTURES

A sum of £20 per annum is being given to the Society for a limited period of years in commemoration of the centenary of the discovery of mercerisation. Suitable lecturers are invited to give a Mercer Lecture annually.

1944 N. G. McCulloch and G. S. Hibbert. "Science in an Old Industry."

1945 G. S. J. White, B.A., and T. Vickerstaff, Ph.D. "Colour."

1946 D. Entwistle, B.Sc., A.R.I.C. "Regenerated Fibres from Natural Polymers."

1947 E. J. Bowen, M.A., F.R.S. "Colour and Constitution— The Absorption of Light by Chemical Compounds."

1948 F. Farrington, B.Sc., F.R.I.C. "Textile Printing."

1949 E. Wilson, B.A. "Some Applications of Chemistry to Textile Finishing."

1950 A. B. Meggy, Ph.D., A.R.I.C. "Some Recent Developments in the Theory of Dyeing."

1951 D. Traill, Ph.D., F.R.I.C., F.T.I. "Some Trials by Ingenious Inquisitive Persons— Regenerated Protein Fibres."

1952 F. C. Wood, M.Sc., Ph.D., F.R.I.C., F.T.I. "Non-felting Wool and Wool Mixtures."

1953 J. R. Blockey, M.Sc., F.R.I.C., and D. H. Tuck, A.L.C. "The Coloration of Leather."

1954 N. W. Yelland, B.Sc., A.R.C.S., D.I.C. "Physics in the Dyeing, Printing, and Finishing Industries."

GEORGE DOUGLAS LECTURE

A sum of £2000 was given to the Society by the Bradford Dyers' Association Ltd., the income from the investment of which is employed in providing a biennial lecture on some subject connected with the colouring or finishing of textiles.

1949 H. Levinstein, M.Sc., Ph.D., M.I.Chem.E., F.R.I.C. "George Douglas, His Times, and Some Thoughts on the Future."

1952 R. Hill, Ph.D. "Synthetic Fibres in Prospect and Retrospect."

1953 T. Holbro, Ph.D. "The Search for New Dyes in relation to Modern Developments in the Textile Field."

Proceedings of the Society

The Basic Mechanisms of Dye Absorption during Pad-dyeing

H. B. MANN

One-day Symposium on Continuous Dyeing held by the Manchester Section at the Manchester College of Technology on 19th March 1954, Mr. J. Boulton in the chair

A study of the basic mechanisms of dye absorption during pad-dyeing has shown that direct dyes are taken up by viscose rayon filament and staple fabrics in two ways—(*a*) adsorbed at the surface of the individual filaments, and (*b*) in dye solution mechanically held within the fabric structure.

A differential absorption of dye and water has been clearly demonstrated. This must always be present in principle, although it may become overshadowed by substantive dyeing of the fibre at high padding temperatures or after prolonged immersion in the dyebath.

1. INTRODUCTION

During recent years there has been a growing tendency to adopt wherever possible what may be termed "continuous" methods for dyeing and processing textiles. Such methods have the merits of saving time and producing a uniform result, although they have the disadvantage, especially in the case of continuous dyeing, that it is necessary to process a very considerable yardage of any given fabric and colour in order to justify the initial high cost of the plant and the time required in "setting up", and to ensure that any end-to-end shade variations can be ignored.

In such continuous processing methods the basic operation which is common to all is that usually described as *padding*. This comprises passing the carefully scoured fabric in open width through a small trough containing the processing solution and then removing the excess solution by passing between positively driven, loaded rollers, which constitute the *pad mangle*. Alternatively, in the molten-metal machine the fabric passes through a shallow pool of dye solution, the excess being removed by the squeezing pressure of the molten metal. In general, the dye is then fixed by a hot, moist treatment intended to promote diffusion of the dye molecules from the surface to the interior of the filaments of the yarn.

The final result, whether it be the quality of the dyeing or the general standard of any other treatment, will depend primarily upon the success achieved during this padding operation. A considerable amount of technical information has already been published on methods of continuous dyeing [1–7], but very little is known about the basic mechanisms of the general padding process, in spite of their obvious importance. It was considered that a study of these mechanisms was timely in view of the current widespread interest in such continuous methods of processing.

The present paper deals solely with continuous dyeing processes and is concerned primarily with the application of direct dyes to viscose rayon. The basic principles which have been observed are, however, applicable to all other systems in which a fabric is impregnated with a solution and the active component is fixed either by drying or by steaming after removal of the excess liquor. The relative importance of the various factors will, of course, depend both on the nature of the fabric and on the components of the padding bath, but the differential effects recorded here will always be present, even if small, unless the rates of diffusion of solvent and solute into the fibre are equal. This is very unlikely in any of the technical processes to which textile fabrics in general are subjected.

2. EXPERIMENTAL MATERIALS

Cellulose

REGENERATED CELLULOSE SHEET—Standard 600-quality Cellophane (British Cellophane Ltd.)—Thickness 4×10^{-3} cm.

CONTINUOUS-FILAMENT VISCOSE RAYON YARNS—Current production of 100/40, 150/40, 300/50*.

VISCOSE RAYON STAPLE-FIBRE FABRICS—1½ denier, 1 $\frac{7}{16}$ in. staple; 4½ denier, 6 in. staple.

Dyes

Sky Blue FF (*C.I.* 518) and Violet R (*C.I.* 388).

The plasticising glycerol was removed from the Cellophane by repeated washing in distilled water. The yarns and fabrics, too, were thoroughly scoured (0·5% soap, 1 c.c. ammonia (sp. gr. 0·88) per litre) and rinsed in distilled water before use to remove any spinning lubricant or size.

All the materials used were conditioned at 65% R.H., and therefore had an initial moisture regain of ca. 13%.

The above two dyes were chosen because of their known constitutions and wide variation in diffusion coefficients in viscose rayon under conventional dyeing conditions. They were obtained in an electrolyte-free state by extraction with aqueous ethanol followed by further purification by ion-exchange techniques; their subsequent purity was checked by determination of the sulphated ash content and conductimetric titration for chloride.

3. EXPERIMENTAL PROCEDURE

Complete details of the experimental technique adopted for impregnating both the Cellophane sheet and the continuous filament yarns have been described elsewhere [8], but it will be convenient to recall the essentials of the method here.

* A viscose rayon yarn 9000 metres of which weighs 100 g. and which is composed of 40 filaments is briefly described as 100/40 viscose. The twist in these yarns is very low, ca. 1 t.p.in., so that the individual filaments are relatively free.

The Cellophane sheet was merely immersed in the appropriate solution for a selected period, the excess solution removed by careful blotting between sheets of blotting paper, and the impregnated material analysed—the water absorption by weighing and the dye content colorimetrically.

For the yarns the procedure consisted in padding, mangling, collecting, and finally analysing the treated yarn, this series of processes being carried out on a single end of yarn. In this method there are two main points of interest—(1) The period of immersion in the padding bath was varied by passing the yarn a differing number of times around a hollow glass roller immersed in the padding bath and thence to the mangle. The wetting time, taken as the total time elapsing between the yarn entering the solution and the mangle nip, is easily calculable from the mangle speed and the length of the wetted yarn. (2) In order to ensure complete removal of surplus liquor from the surface of the yarn, it was necessary to cover the mangle rolls with two thicknesses of a viscose rayon staple fabric. It was subsequently found that the surplus liquor was removed from the yarn more efficiently if the fabric used to cover the mangle rolls was impregnated with a dilute solution of a wetting agent (Teepol (Shell), 1 ml./litre), dried, and conditioned before use. This technique had some advantages over the initial procedure, in which the wetting agent was added to the bath, when a slight scum tended to form on the surface of baths containing strong solutions of electrolytes. It should be noted that the addition of the wetting agent was made, not to improve the wetting of the yarn under test, but to aid removal of the surplus liquor. A higher equilibrium absorption and a slightly higher apparent rate of wetting were observed in the absence of the wetting agent, owing to the inefficient removal of surplus liquor.

For impregnation of the fabric, the technique, while basically similar to that used for the yarn, necessarily differed in a number of ways. The wetting time was varied by passing a narrow strip (1½ in. wide) of the fabric around a given number of small brass rollers mounted at opposite sides of a light steel framework, and thence to the mangle nip. The complete framework unit was immersed in the dyebath, and the wetting time was again calculable from fabric path length and mangle speed.

For the shortest wetting time (ca. 0·1 sec.) a technique similar to that used in the so called "nip padding" was adopted. In this process the passage of the fabric through the padding trough is eliminated, and the only impregnation which the fabric receives is from the liquid remaining immediately behind the nip, which in technical practice is furnished by the lower roller (sometimes felt-covered) running, partly submerged, in the padding liquor. For these experiments the padding solution was merely allowed to flow slowly on to the top roller immediately above the point at which the fabric entered the nip of the mangle.

A three-bowl mangle was used having rollers of 4 in. diameter covered with rubber of 80° Shore hardness; the loading was 50 lb. per inch width of roll.

4. DISCUSSIONS AND RESULTS

(*a*) *General Considerations*

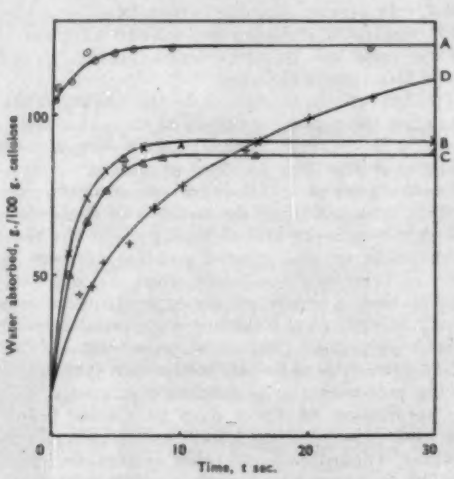
In the present work attention has been concentrated upon the absorption of the various components of the dyebath, especially the dependence of the relative amounts absorbed upon the principal variables of the system—time of immersion, temperature, dyebath constitution, etc. From the results it has been possible to obtain a fairly comprehensive picture of what takes place when a fabric is subjected to the process of padding, and the basic mechanisms of dye absorption can now be more clearly defined than was hitherto possible.

When a fabric is immersed in water and then passed through a mangle to remove some of the excess, it is clear that a considerable proportion of the water which is retained is held mechanically in the fabric structure. It was felt that such a system was too complicated to consider in the initial experiments. Accordingly, experiments were first carried out on regenerated cellulose sheet (in which the complications of mechanically held liquid are absent) and single ends of continuous-filament yarn (when such effects are very small). By this means the rôle of the substrate itself in the absorption process could be investigated.

The bulk of this work has already been published in detail [8], but a summary of the main points of interest is given here, since they are essential for an understanding of the results which have since been obtained with simple woven fabrics.

(*b*) *The Absorption of Water by Viscose Cellulose*

Measurement of the rate of absorption of water by dry viscose cellulose has shown that it is a relatively rapid process requiring some 8–10 sec. for completion at room temperature in the case of yarns of normal technical importance.



A —○— 1½-denier viscose rayon staple-fibre fabric
B —×— 150/40 viscose rayon
C —△— 300/50 viscose rayon
D —+— Regenerated cellulose sheet

FIG. 1—Dependence of Water Sorption on Time at 20°C.

The rate of absorption is strongly temperature-dependent and requires an activation energy of some 7 kcal./mole. This rate of wetting varies also with the surface area of the fibres, as can be seen from Fig. 1, in which the rate-of-wetting curves for two yarns (3·75 and 6 denier per filament) and regenerated cellulose sheet are reproduced.

These and other data, not given here, suggest that the rate of wetting is approximately proportional to the specific surface area and not to the square of this area as would normally be expected. It is concluded that to account for this effect the smaller filaments must be somewhat tougher than the large filaments and the cellulose sheet.

The rate-of-wetting data for a simple woven fabric are also given in this graph, and will be considered later in more detail in the appropriate section of this paper.

Similar experiments have shown that the course of absorption of simple solutes such as inorganic salts, glycerol, urea, sucrose, etc. from aqueous solution follows a very similar pattern, although the rate constant is, in all cases, smaller than that for the water and shows a strong dependence upon molecular dimensions.

(c) *The Absorption of a Direct Cotton Dye*

The absorption of a direct cotton dye, however, follows a different course from the absorption of water. Initially a small amount of dye is absorbed, but no further dye absorption accompanies the continued absorption of water until the fibres are completely swollen, when the onset of normal substantive dyeing occurs. This effect is reflected in the variation of the ratio of dye to water absorbed, which passes through a well defined minimum.

These effects are illustrated in Fig. 2, which shows the absorption of both water and dye by a standard 100/40 viscose rayon yarn at 20°C., and in Fig. 3, where the ratio of dye to water absorbed is given for regenerated cellulose sheet at 0°, 20°, and 40°C., showing the expected pronounced effect of temperature on the shape of the curve. It should be noted that, if dye and water enter the yarn simultaneously and without preference, the dye : water ratio would be identical with that in the applied dye solution, viz. 0·2 g. dye per 100 g. water.

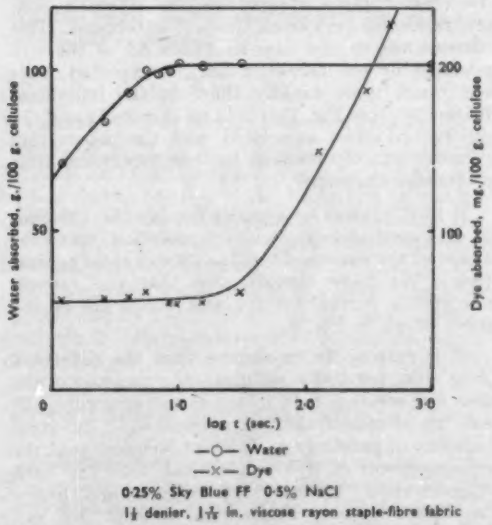


FIG. 2—Absorption of Dye and Water at 20°C.

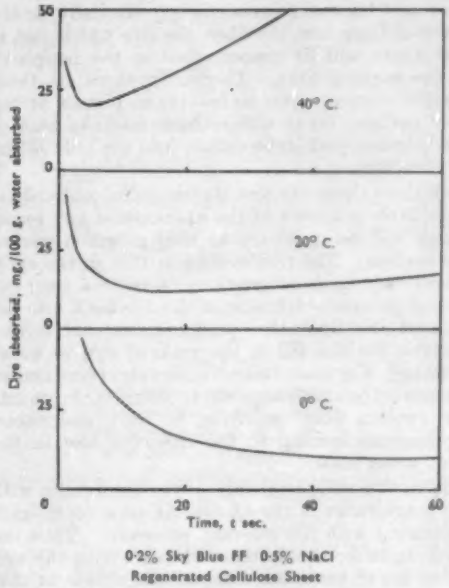


FIG. 3—Absorption of Dye and Water at Various Temperatures

(d) *Working Hypothesis*

All of these effects can be explained, at least qualitatively, by the following simple working hypothesis—

Consider a dry viscose rayon yarn of cross-section (theoretical) *aaa* (Fig. 4). When such a fibre is immersed in an aqueous dyebath, water will diffuse quite rapidly into the bulk of the fibre, which will finally assume the cross-section *bbb*. Let us now consider the dye which was in the water absorbed by the fibre (equivalent to the difference

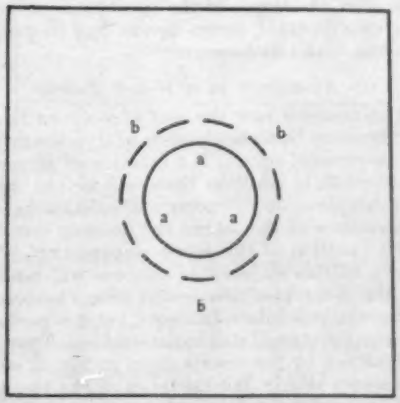


FIG. 4

in area of the two cross-sections). Initially, as the water diffuses into the fibre, the dye which was in this water will be concentrated at the periphery of the swelling fibre. Thereafter, there are three possible courses open to it— (*a*) to remain at the fibre surface, (*b*) to diffuse back into the bulk of the solution, and (*c*) to diffuse into the bulk of the swollen fibre.

Of these three, the first is of doubtful probability, since little is known of the existence of any forces which will be necessary to hold so much dye to the surface. The results suggest that in the early stages (say for impregnations of up to 5 sec.) the second process— diffusion of the dye back into the bulk of the dyebath— predominates and is responsible for the fall in the ratio of dye to water absorbed. For more extended periods of immersion, process (*c*) becomes important, diffusion of dye into the swollen fibre occurring by well understood mechanisms leading to the observed rise in the dye : water ratio.

Both of these predictions are in accordance with the magnitudes of the known diffusion coefficients associated with the relevant processes. Thus the coefficients for the diffusion of direct dyes through water are of the same order of magnitude as that governing the diffusion of water through cellulose (i.e. 10^{-6}–10^{-7} sq.cm./sec.), whilst the diffusion of these same dyes through water-swollen cellulose is at least 10–1000 times slower.

From the results shown in Fig. 3 it is seen that temperature has a pronounced effect upon the general shape of the curve of dye : water ratio against time. Such an effect is again in accordance with the working hypothesis put forward above. Thus the slope of the initial section of the curve is governed by the rate of diffusion of dye through water, which, in turn, will be closely linked with the viscosity of the solution, and it is unlikely that an activation energy of more than 6–7 kcal./mole will be associated with this process. The corresponding slope of the second section of the curve, however, depends upon the diffusion of dye through cellulose, and the corresponding energy term in this process is generally accepted to be at least twice this figure: the average value for a number of direct dyes can be taken as 14 kcal./mole [9]. As can be seen, the slopes of the appropriate sections of the experimental curves are in fact in general agreement with this reasoning.

(*e*) *Absorption by a Woven Fabric*

Let us consider now the case of a woven fabric. Here the same basic mechanism of dye absorption must be present, since it is a function of fibre constitution, but in addition there will be the mechanical complication of excess dye solution held in the interstices of the fabric, the amount certainly being a function of the fabric construction. The presence of this excess dye solution will tend to mask the differential absorption effects associated with the single cellulose filaments, but it is probable that these effects will still be detectable. That this is so is shown by the results given in Fig. 5, which demonstrate clearly the existence of the two processes, viz. diffusion of dye away from the cellulose followed by the slower substantive dyeing effect. The pronounced effect of temperature is again illustrated, and it is probable that as the temperature is further increased the first process, although still present, will be hard to observe. Results obtained at 60°C., not shown here, confirmed this supposition; the effect was just detectable at this temperature with the present experimental procedure, but the magnitude of the substantive dyeing suggested that at, say, 80–90°C. this would predominate and the diffusion of dye back into the solution would pass unnoticed.

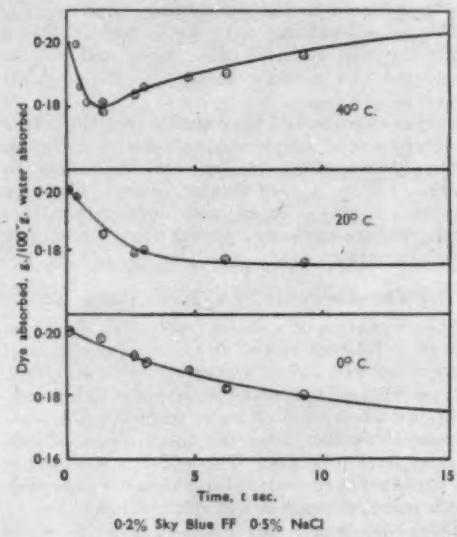
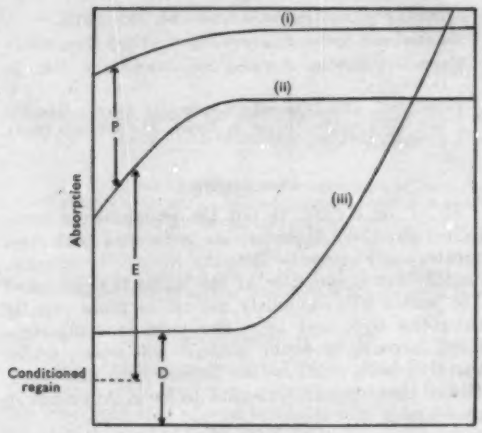


FIG. 5— Absorption of Dye and Water by a Simple Viscose Rayon Staple-fibre Fabric

It is also important to note from Fig. 5 that the dye : water ratio approaches the dyebath concentration for very small times of immersion. This corresponds to the case in which all of the dye retained by the fabric (which, as expected, wets out much more rapidly than do the individual filaments— see Fig. 1) is held mechanically and the differential effect associated with the penetration of water into the cellulose has had insufficient time to become apparent.

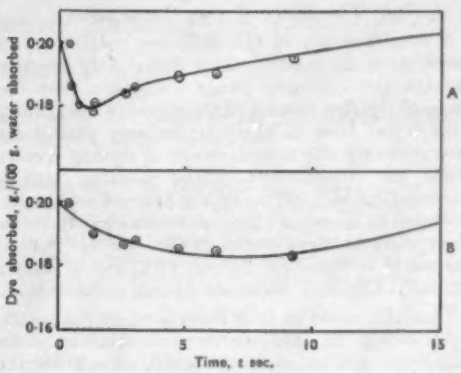
It is of interest to consider further the influence of the mechanically held dye solution upon the shape of the curves of the dye : water ratio against time. We have already seen that the rate-of-absorption curves for dye and water are of the form shown in Fig. 6.

It is reasonable to assume that the difference *P* (g. soln. per 100 g. cellulose) is a measure of the free dye solution held in the fabric structure. It can be demonstrated experimentally, by comparisons of paddings at different weights, that the concentration of dye is identical with the bath concentration, at least for medium and longer immersion times. From this concept we can deduce certain quantitative relations.



(i) Water–fabric
(ii) Water–fibre
(iii) Dye–fibre

FIG. 6— General Form of Absorption Data



0·2% Sky Blue FF 0·5% NaCl
Viscose rayon staple-fibre fabrics
A 1½ denier, 1 7/16 in. staple
B 4½ denier, 6 in. staple

FIG. 7— Effect of Fabric Construction on Dye and Water absorbed at 40°C.

At any time t let—

P_t = Excess imbibition of fabric over fibre (g. H_2O/100 g. cellulose)

E_t = Excess imbibition of fabric over conditioned regain (g. H_2O/100 g. cellulose)

C = Bath concentration of dye (g./g. H_2O)

D_t = Dye on fibre (g. dye/100 g. cellulose)

R = Dye : water ratio in fabric (g. dye/g. H_2O absorbed)

Then—

$$R = \frac{D_t + P_t(C + a_t)}{100E_t}$$

where a_t is the excess of dye concentration in the free water within the fabric at very short immersion times— when the excess had not had time to diffuse out of the fabric. The quantity a_t is in any case small, and at medium and longer times the simpler expression—

$$R = \frac{D_t + P_tC}{100E_t}$$

is accurate, and at shorter times nearly accurate.

Since D_t is found by experiment to be constant for short and medium times, it is clear that R tends to fall during these periods, beginning to rise at longer immersion times, when D_t increases as the fibres absorb dye from the interstitial solution by a normal substantive mechanism.

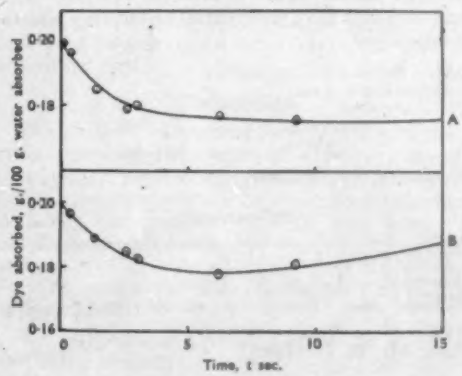
A minimum value of R has been observed experimentally with both yarns and fabrics, although the P_tC factor tends to reduce the depth of the trough.

(f) *The Effects of Fabric Construction and Yarn Denier*

A combination of the two effects mentioned in the previous section is no doubt responsible for the considerable variation in shape of the two curves given in Fig. 7. These results were obtained under the same general conditions, except that in one case the fabric was woven from 1½ denier, 1 7/16 in. staple viscose rayon and in the other from 4½ denier, 6 in. staple yarn.

It was the original intention to illustrate merely the effect of yarn denier, which may be expected to manifest itself by a decrease both in the amount of dye initially absorbed by the yarn and in the rate of absorption of water, these effects leading to a deeper but broader minimum in the curve of dye : water ratio against time.

In fact, the broadening of the minimum is demonstrated to a very considerable extent, but it seems probable that it has been exaggerated somewhat by a diminution in the excess dye solution factor P. The inclusion of this effect was unavoidable, since two fabrics alike in every detail except filament denier were not available.



0·2% dye 0·5% NaCl
1½ denier, 1 7/16 in. viscose rayon staple-fibre fabric
A Sky Blue FF B Violet R

FIG. 8— Effect of Dye Constitution on Dye and Water absorbed at 20°C.

(*g*) *The Effect of Dye Constitution*

A consideration of the diffusion coefficients of direct dyes in water—they differ only slightly through the complete range—suggests that the shape of the first section of the curve of dye : water ratio *versus* time is likely to be very similar for dyes covering the normal range of dyeing speeds. When the temperature of the padding bath is increased to, say, 60°C., or the time of immersion extended to 15 sec., a highly undesirable differential absorption of dyes could occur by the normal process of substantive dyeing with, say, a binary mixture of dyes of dissimilar dyeing properties.

That this could be so is illustrated by the results given in Fig. 8. The curves were obtained under conditions similar in every detail, except for the use of dyes of differing dyeing speeds. The two dyes differ in dyeing rate on viscose rayon at 90°C. by a factor of ca. 30, and yet at 20°C. the amount of dye absorbed is not significantly different for times of immersion of less than 7–8 sec.; it is only for longer times that appreciable differences in absorption occur, as the substantivity factor becomes of importance.

(*h*) *Technical Importance*

The observations detailed in this paper show that the amount of dye taken up by a fabric on padding may differ considerably from the amount calculated simply from the water take-up and bath concentrations. Whilst it has been generally accepted that the dye absorption could be higher than that calculated because of substantive dyeing, it is now shown that the dye absorption can also be lower than calculated if the time of immersion and the temperature are such that the effect of the substantive dyeing process is small.

It is concluded that the time of padding of a staple or filament viscose rayon fabric should be the smallest possible consistent with uniform and thorough wetting, and that the temperature should be kept as low as possible consistent with solubility of dye and wetting of the fabric. This will ensure that mechanical pick-up of dye solution predominates and that preferential absorption effects are minimised.

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Discussion

Mr. J. J. RYAN: Is not the phenomenon mentioned by Mr. Mann to be expected with two substances of greatly differing molecular weights, namely water and dye, at the same temperature? The water will obviously diffuse in more rapidly than the dye, and once the yarn is completely filled increase in water content will cease, whilst the dye will continue to diffuse into the yarn. Hence there is surely bound to be a minimum in the curves.

Mr. MANN: I would agree entirely that the phenomenon of preferential absorption of water in the early stages of impregnation is precisely what must be expected when a textile fibre is immersed in a solution the components of which diffuse into the cellulose at dissimilar rates. The purpose of the present paper was to demonstrate these basic mechanisms of dye absorption in pad dyeing and to show that preferential absorption of either dye or water may be observed depending upon the conditions used.

Mr. C. DUCKWORTH: The curves which show a slower rate of diffusion for soluble dye compared with that of the water itself indicate a negative take-up of dye. One would expect a dispersion or suspension of an insoluble pigment to diffuse even more slowly, and yet pigment padding does not show significant tailing or build-up. How is this anomaly explained?

Mr. L. W. C. MILES: Although it may be common experience that tailing does not occur in pigment padding, it certainly can occur. With a large liquor bath, which was not replenished, a closely woven viscose rayon fabric padded at 60°C., through a dispersion of a Paste Fine dye without a wetting agent, showed a very appreciable increase in depth as the run proceeded.

Mr. MANN: We have not extended our work to the absorption of dispersions or suspensions, but I would agree that the rate of diffusion into cellulose of such particles would be even slower than that of large direct dye molecules. It is probable, however, that the diffusion of the particles away from the fibres back into the bath is also much slower, and it is possible that only under somewhat unusual conditions of impregnation will differential absorption effects be observed in practice. The remarks of Mr. Miles would seem to support this.

Affinity Effects during Padding

W. J. MARSHALL

One-day Symposium on Continuous Dyeing held by the Manchester Section at the Manchester College of Technology on 19th March 1954, Mr. G. S. J. White in the chair

The advantages and disadvantages of continuous dyeing methods are briefly discussed. A factor of great importance in these processes is the change in colour during the initial period of the run, which makes shade matching and running to shade a matter of considerable skill. This is due to the change in concentration of the pad liquor caused by the affinity of the dye and similar effects. Assuming the simplest possible relations, the magnitude of this change has been calculated, and measurements of a practical system have shown that this mathematical treatment is adequate to characterise the system. Finally, the practical significance of this work is discussed.

Introduction

In the continuous dyeing of piece goods, we are concerned with applying colouring matter to the fabric so that it is placed mechanically close to its final position in the fully dyed cloth. The impregnated material is then treated in such a manner that the dye is fixed *in situ*. As a result, extremely short dyeing periods can be employed, because levelling of the dye is not required and, in fact, is not wanted. For example, dyeings fully equal in wet fastness, etc. to conventional ones are obtained with dyeing times of less than 4 min. for direct and 30 sec. for vat dyes, and yet this technique is probably the best method of covering irregularities in rayon staple fibre fabrics introduced by weaving variations, because the mechanical impregnation ensures that each portion of the cloth receives only its quota of dye. It follows that the ideal continuous dyeing system consists of a stage of purely mechanical application of the dye without affinity followed by rapid fixation *in situ*. In practice, this ideal system is difficult to achieve, but the "pad–steam" method of dyeing vat dyes, where a pigment pad is followed by a chemical pad and steam fixation, approaches this ideal closely. Even here, however, bleed-off of the pigment pad into the chemical pad is a source of "tailing", and in practice this is overcome by adding to the latter an arbitrary proportion of the pigment-padding liquor. In the case of direct and leuco vat dyes, it is common knowledge that padding is usually accompanied by a greater pick-up of dye than corresponds to the liquor absorbed. This is due to the affinity of the dye for the fabric, which is actually being dyed during the time it is being padded. The extent to which dyeing takes place may be considerable. Thus, when one looks at the rate of dyeing of a typical direct dye, it is found that Durazol Fast Yellow 6G takes 30 sec. to reach 50% exhaustion in a conventional dyeing[1], while Lemin, Vickers, and Vickerstaff[2] showed the time of half-dyeing to be between 5 and 25 sec. for a series of dyes in which the dyeings were carried out with a short liquor length.

An effect which is essentially similar to this is encountered in repadding wet fabrics, as in the wet process of the pad–steam application of vat dyes. The fabric is pigment- and then chemical-padded without the intermediate costly drying. In the chemical pad liquor, however, dilution of the pad liquor occurs, and more solute (this time sodium hydrosulphite plus caustic soda) is taken up by the cloth than that corresponding to the pick-up difference. In this case, there has been an interchange between the chemical pad liquor and the wet fabric, which reaches its greatest effect when the second padding mangle is adjusted to give the same expression as the first, so that there is no net liquor pick-up from the second trough.

As a result of these effects, due to "affinity" in the first case and "dilution" in the second, the concentration of the liquor in the padding trough falls at the beginning of the run, and the fabric suffers a corresponding variation in colour. The success of these methods in practice depends completely on the skill of the dyer in adjusting his conditions to minimise the colour changes. Ideally, these should be made to give a precise balance between the amount of dye fed into the system in the feed liquor and the amount of dye leaving it on the cloth.

Thus, the advantages of continuous dyeing methods must be weighed against the inherent difficulties in control and shade matching. All these remarks apply with even greater force to dyeing in the Williams unit and its precursor, the roller vat system. It is, therefore, well worthwhile to examine the problem introduced by the affinity effect during padding. The present discussion is the first step in making a detailed analysis of the problem, so that differences between dyeing systems and between dyes can be readily characterised, and thus a method of obtaining the optimum padding conditions and a rational basis for comparing dyes can be worked out.

Theoretical

The problem which must be solved is how much cloth must be run before a uniform colour is obtained, or, expressed in another way, how long it takes a padding system to come to equilibrium. Although the specific case dealt with here is a simple padding operation, the method of treatment and many of the conclusions apply equally to other systems, such as the molten-metal machine and the Williams unit.

We will consider a padding system in which the pad liquor contains dye initially at the same concentration as that with which it is fed, viz. C_f g./litre; i.e. the starting and feeding concentrations are equal. The rate of feed (v litres/min.) depends on the rate of passage of the cloth, etc., and to keep a constant liquor level in the pad trough, this must

equal exactly the rate at which liquor is removed by the cloth—

$$\text{Feed rate } (v) = \text{Cloth weight } (W) \text{ per unit length} \times \frac{\%\ \text{Pick-up } (P)}{100} \times \text{Running speed } (S)$$

or

$$v = \frac{WPS}{100} \qquad \text{(i)}$$

The amount of dye contained in this liquor is mechanically applied to the cloth, but in those cases mentioned earlier when dyeing takes place in the pad trough, the actual pick-up of dye by the cloth will exceed the mechanical pick-up. We can write this down quantitatively by saying that the actual dye pick-up is x times as great as the mechanical pick-up: when $x = 1$ there is no effect; when $x = 1{\cdot}5$, the cloth picks up 50% more dye than the amount contained originally in the liquor picked up; and so on. This removal of dye in excess of that which enters the trough in the feed liquor causes the concentration to fall, which in turn reduces the amount taken up by the fibre, until a final equilibrium is reached at which the amount of dye being taken out by the cloth equals that entering the trough in the feed liquor—

$$\left[\begin{array}{c}\text{Rate of change}\\ \text{of dye content}\\ \text{in pad liquor}\end{array}\right] = \left[\begin{array}{c}\text{Rate at which}\\ \text{dye enters}\\ \text{the trough}\end{array}\right] - \left[\begin{array}{c}\text{Rate at which}\\ \text{dye is}\\ \text{removed from}\\ \text{the trough}\end{array}\right]$$

$$V\frac{dC}{dt} = vC_f - xvC$$

where C is the concentration in the pad trough at time t and V is the volume of pad liquor in the trough. Thus the rate of change of concentration in the padding trough is—

$$\frac{dC}{dt} = \frac{v}{V}(C_f - xC)$$

from which, assuming x to be constant –

$$\frac{C}{C_f} = \frac{1}{x}\left[1 + (x-1)e^{-xtv/V}\right] \qquad \text{(ii)}$$

It can be seen that the concentration of the liquor in the padding trough depends on—

(*a*) The value of the affinity factor x, and

(*b*) The value of tv/V.

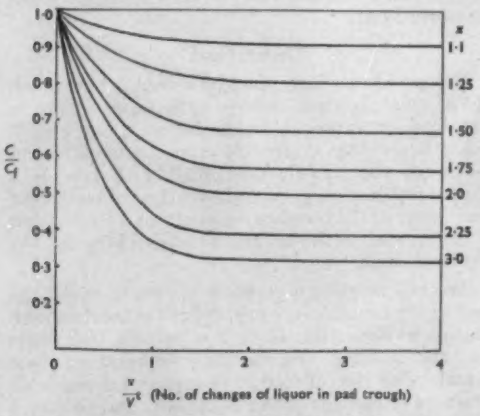

FIG. 1—Effect of Feed Rate, Trough Volume, and Affinity Factor on the Rate at which Equilibrium is approached

Thus if we draw the graph of C/C_f against tv/V as in Fig. 1, we can readily find how quickly a given system comes to equilibrium by simply changing the scale according to the values of v and V. The value of C/C_f may be taken as the relative change in depth of the final dyed material. This falls rapidly in the initial stages, and then comes to equilibrium when tv/V is between 2 and 3.

The larger the value of x, the greater is the change in depth, and in fact the initial depth is x times as great as the final equilibrium value, as can be shown by substituting in equation (ii) for $t = \infty$. Thus if $x = 1{\cdot}5$, the first material through is 1·5 times the strength of the true depth; i.e. the run must be started with the dyeing 50% strong. Of course, the experienced dyer avoids this by adding water to his pad trough before starting the run. The amount added is that found by experience to be effective: in other words, he makes a guess based upon personal experience. But in mixture dyeings, dyes with different values of the "affinity factor" x require different degrees of dilution; thus the pad liquor must be corrected not only for concentration but also for the relative proportions of the individual dyes.

When it is known that the dyes used are subject to large "affinity effects", it is futile to attempt shade correction until approximate equilibrium is reached. It also appears that the normal method of pitching shades by padding through a pad liquor, whose composition is then translated to the recipe for feed liquor, is bound to give erroneous results whenever the value of x is greater than 1·1. It is therefore essential on these grounds alone to relate these results to practical systems.

TIME REQUIRED TO REACH EQUILIBRIUM

(*a*) *Effect of "Affinity Factor" x*

From Fig. 1 it can be seen that, while large values of x correspond to large changes in depth, these curves come to equilibrium at least as rapidly as those for a smaller value of x. To calculate how quickly equilibrium is reached it is better to refer to the final or equilibrium depth rather than to the initial one as in equation (ii). Thus the fractional difference from the final depth is given by—

$$\frac{C}{C_\infty} - 1 = (x-1)e^{-xtv/V} \qquad \text{(iii)}$$

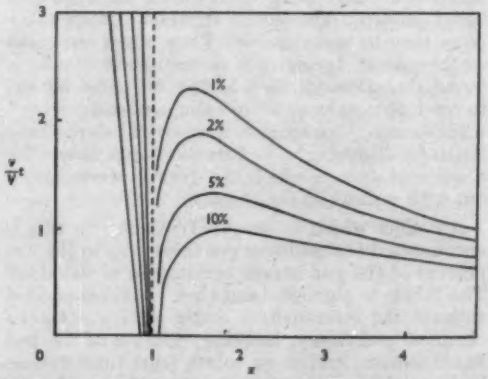

FIG. 2—Relation between Affinity Factor x and Time required to approach Equilibrium (within 1%, 2%, 5%, and 10%)

and the percentage difference is 100 times this value. We may regard equilibrium as being reached when the difference has become, say, 5% of the final depth (both sides of equation (iii) having the numerical value 0·05), and the effect of x on the time to reach that particular difference has been calculated. The results, together with the curves corresponding to differences of 1%, 2%, and 10%, are plotted in Fig. 2. It can be seen that for, say, the 5% curve, the time is relatively independent of the value of x except at the beginning of the curve, i.e. $x < 1{\cdot}05$. This applies only to values of $x > 1$; for values of $x < 1$ the time to reach equilibrium is not only highly dependent on x but also very much greater. These results for $x > 1$ may be expressed in the form of a table (Table I).

TABLE I

Time required to approach Equilibrium in the Padding Trough

(for $x > 1$)

$\left(\frac{C}{C_\infty} - 1\right) \times 100$, % ...	1	2	5	10
$\frac{v}{V}t$	1·8–2·6	1·5–2·2	1·2–1·6	1·0–1·3

(b) Effect of Padding System

In the previous discussion it will have been noted that tv/V, the non-dimensional parameter characterising the rate of attainment of equilibrium, has been used as synonymous with time. In fact, tv/V represents the number of times the volume of liquor contained in the pad trough has been replaced, and represents a definite amount of cloth. It is therefore immediately obvious that the following factors will affect the actual time required to reach equilibrium—

(1) The pad trough volume V—the time is proportional to the volume.

(2) The feed rate v—the greater the feed rate, the shorter the time required to reach equilibrium. The feed rate can be effectively increased only by reducing the mangle squeeze and so giving a larger pick-up. Increasing the running speed reduces the time to reach equilibrium, but the amount of cloth run remains unaltered; the ending will, however, be reduced by virtue of the lower value of x due to the shorter padding time.

To illustrate these conclusions, Table II has been prepared.

TABLE II

Yardage required to ensure Consistency of Depth

(Consistency of depth within 5%)

($x > 1$; $tv/V = 1{\cdot}5$)

Typical cloth...	4-oz. Poplin	8-oz. Cotton Twill			12-oz. Duck
Mangle expression...	50%	60%	100%	150%*	100%
Pad Trough Capacity					
40 gal.	5000	2000	1200	—	800
10 gal.	1200	500	300	—	200
2 gal.	240	100	60	40	40

* Typical value for the molten-metal machine

Where one wishes to reach finality of colour quickly, the overwhelming advantage of a small padding trough is clear, and this is an excellent illustration of one of the major advantages of the Standfast molten-metal machine. It should be noted that the very large liquor pick-up is an additional advantage in this respect.

Experimental

APPARATUS

To obtain experimental evidence on values of x which are encountered in practice, a small Perspex padding trough was made, and this was attached to a domestic washing-machine mangle driven by an electric motor with a variable-speed drive.

The trough was of **U** shape approx. 1 cm. wide and of sufficient depth to give a 6-in. immersion length in the liquor; there was a further distance of 6 in. before the nip, giving an overall padding distance of 12 in. The inside could be withdrawn in order to remove the bottom roller (stainless steel) to facilitate threading. It was made to take cloth 3 in. wide, and held 80 ml. of dye liquor under running conditions.

The liquor level had to be kept constant, and with such a small surface area as in this trough the feed rate had to be adjusted to 60 ± 1 ml./min. It was found impossible to control this manually, and a constant-level device was made using a Tektor† proximity switch and a magnetically operated glass valve. The simplest method was to use an external level tube, otherwise the balance was upset during running. The valve was a ground-in glass plug which was lifted by a steel rod attached to the armature of a Post Office type of relay. This arrangement allowed $\frac{1}{16}$ in. movement, and gave a sufficiently high flow rate when opened and complete cut-off when closed. With this system only 20 ma. control current was required, thus eliminating one of the disadvantages usually associated with magnetic valves.

No temperature control was found necessary, as the upper temperature was limited to 65°C. by the Perspex trough. However, temperature measurements were made during the run by reading the temperature of the feed liquor in the normal way and measuring the temperature drop between the feed liquor and the pad trough with a thermocouple (copper–constantan).

The overall dimensions of the apparatus are compared with a full-scale machine for 36-in. cloth in Table III. This comparison is based on a running speed of 6 and 30 yd./min. respectively to give a performance which is closely related.

TABLE III

Dimensions and Performance of the Padding Trough in relation to a Typical Full-scale Process under Running Conditions

Variable	Laboratory Trough	Full-scale Trough
Cloth width ...	3 in.	36 in.
Trough width ...	3½ in.	45 in.
Capacity ...	80 ml.	5 gal.
Dimensions to liquor level ...	1 × 8 × 10 cm.	2 × 45 × 15 in.
Running speed	6 yd./min.	30 yd./min.
Padding length	12 in.	60 in.
Immersion length	6 in.	30 in.
Padding time ...	3·3 sec.	3·3 sec.
Immersion time	1·7 sec.	1·7 sec.
Length to be run to give tv/V = 1·5	12 yd.	300 yd.

† Fielden Electronics Ltd.

METHOD

An experiment was carried out by running through the trough sufficient cloth to give equilibrium. Samples of dye liquor were abstracted at suitable intervals with a hypodermic syringe. These were then diluted by means of an Agla* micrometer syringe and estimated optically using either the Unicam SP 600 spectrophotometer or the Cary spectrophotometer. Liquor pick-up was measured by weighing the cloth before and after padding and checked by measuring the total volume of liquor used. The dyes used were the normal commercial products, and these will be further discussed with the results.

Results

FIT OF EXPERIMENTAL RESULTS TO EQUATION

The first point of interest is the extent of agreement between fact and theory. Typical results are given in Fig. 3 for Chlorazol Sky Blue FF 200 and Chlorazol Fast Scarlet 8 BS. In this the concentration has been plotted against the function tv/V. The best fit to the theoretical curve was obtained, and the full lines are the theoretical curves (of equation (ii)) for $x = 1{\cdot}35$ and $1{\cdot}13$ respectively. It can be seen that the fit of the points to the curve is very satisfactory, and in fact is as good as scatter of the points will allow.

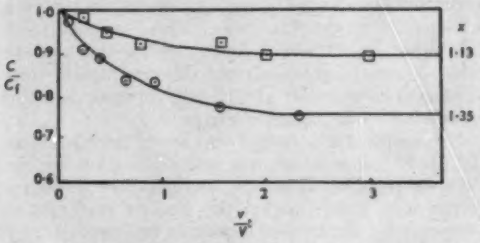

FIG. 3—Fit of Theoretical Equation to Typical Results

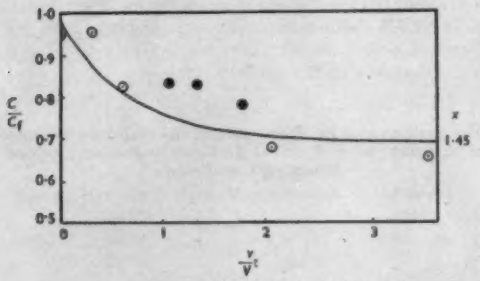

FIG. 4—Effect of Overfeeding during Padding

Early in these experiments it was evident that level control was important, and Fig. 4 illustrates this. During this run gross flooding occurred and dye liquor overflowed. As a result, the dye concentration fluctuated violently. This illustrates the importance of level control in dyeing to a uniform shade.

In all the results obtained so far, curves obeying equation (ii) give a good fit to the experimental points. The value of x, therefore, characterises the system, and it can be used as a parameter to describe variations in behaviour between dyes and the effects of altering the temperature and concentration or adding salt, etc. On the other hand, it can be used as a method of determining the effects on ending of padding variables such as nip pressure, padding time, trough volume, etc.

EFFECTS OF SALT AND BRAND OF DYE USED

As is well known, salt is normally used for standardising direct dyes, except those used for printing. With the latter the maximum solubility is required, and as this applies also to pad–steam dyeing, the printing brands are usually recommended, although it does not follow that all dyes suitable for printing are suitable for continuous dyeing. The presence of salt, as well as lowering the solubility, also increases the final exhaustion and the rate at which the dye is absorbed on to the fabric. This is illustrated in the comparison of the behaviour of the P and S brands of Durazol Blue 2 GN in Fig. 5. Both experiments were carried out at a dye concentration equivalent to 10 g. of the S brand per litre. Thus the padding solution contained, per litre, in the one case 3·5 g. of Durazol Blue 2 GNP, and in the case of the S material it also contained 6·5 g. of diluent salt. This latter corresponds to 20% on the weight of the material in a conventional dyeing, so it is not surprising that the large difference observed should exist between the different brands. The effect of salt is therefore considerable.

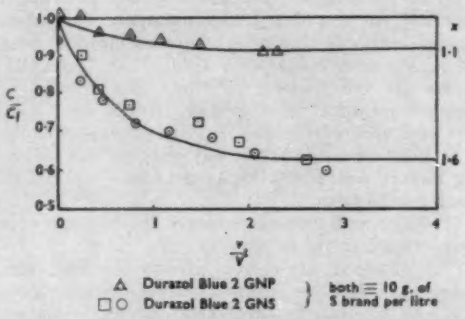

FIG. 5—Effect of Diluent on Affinity Factor for Durazol Blue 2GN

VARIATION BETWEEN DIFFERENT DYES

A small group of dyes have been examined to see how widely they varied among themselves under similar conditions. The material used was bleached cotton drill at a pick-up of 69–71% and at temperatures in the neighbourhood of 60°C. All the dyes were used at a concentration equivalent to 10 g. of the standard strength per litre, with a padding time of 3·3 sec. The results are given in Table IV.

* Burroughs Wellcome & Co.

TABLE IV

Typical Values of x for Various Direct Dyes

Dye	Temp. (°c.)	x	Error in Depth at Start (Ending, %)
Durazol Yellow 4GS ...	59	1·20	20
Durazol Orange RS ...	53	1·14	14
Durazol Scarlet 2GS ...	60	1·3	30
Chlorazol Scarlet 8BS ...	60	1·13	13
Chlorazol Sky Blue FF 200	60	1·35	35
Durazol Blue 2GNP ...	59	1·12	12
Durazol Blue 2GNS ...	64	1·60	60
Durazol Grey VGS ...	62	1·08	8

The error in depth at the beginning of the run may be considerable, but varies greatly from dye to dye. By judicious dilution the ending can be eliminated completely, the proportion of water which must be added to the liquor in the pad trough to achieve this being the same as the error in depth.

VARIATIONS DUE TO FABRIC PICK-UP AND CONCENTRATION

The magnitude of the changes in depth on ending is affected also by the type of material, the amount of liquor picked up by the cloth, and the concentration of the dye (Fig. 6 and 7). It will be seen from Fig. 6 that viscose rayon staple gives a very much smaller concentration change ($x = 1{\cdot}03$) than the cotton drill ($x = 1{\cdot}60$). Part of this effect, however, is undoubtedly due to the higher liquor pick-up (85% as against 70% for the drill), and the value of x is reduced to 1·30 for the drill when the mangle squeeze is reduced to give a pick-up of 76%—a much greater change than might have been expected.

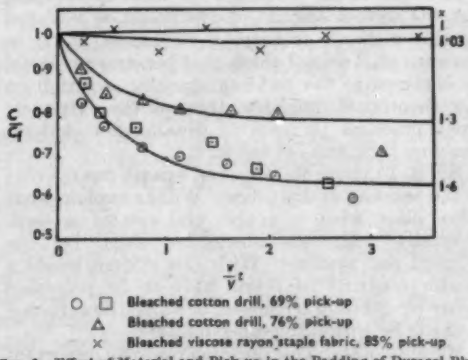

FIG. 6—Effect of Material and Pick-up in the Padding of Durazol Blue 2GNS (10 g./litre)

Fig. 7 shows that the effect of concentration also is considerable. In this comparison changing the concentration of the feed liquor from 10 to 1 g./litre increases the value of x from 1·03 to 1·25. A similar increase is obtained for cotton drill, the figures being from 1·60 to 2·2. This is rather an interesting observation, because it would not have been expected on theoretical grounds unless the dye were highly aggregated or the fibre surface were approaching saturation. A study of this problem in relation to aggregation, solubility, and salt concentration would therefore have an extremely important bearing on the theory of dyeing and on the practical application of dyes under these conditions.

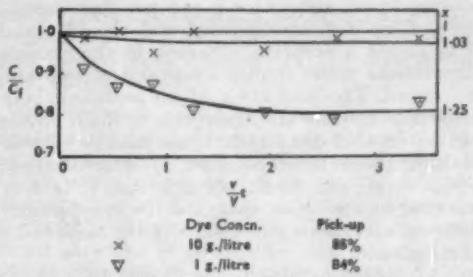

FIG. 7—Effect of Concentration in the Padding of Durazol Blue 2GNS on Bleached Viscose Rayon Staple Fabric

Discussion

THE NATURE OF THE "AFFINITY FACTOR" x

While the affinity factor is an extremely useful and convenient parameter, it has considerable complexity, for it is not a simple property of the dye. Its value depends on a number of factors, and these can be divided into those determined by the dye and those arising from the padding system, the nature of the fabric construction, and the properties of the fibre. The difficulty of calculating its value arises from a lack of fundamental knowledge of the properties of dyes at the high concentrations used in continuous dyeing and the difficulty of treating quantitatively factors such as the turbulence in the pad trough. There is therefore little point in attempting at this stage to evolve a relatively elaborate theory until there is a sufficient fund of factual knowledge on which it can be based and the experimental evidence to confirm or refute the conclusions. One interesting point does, however, arise. Lemin, Vickers, and Vickerstaff[2] have measured the rate of dyeing in short liquor lengths of a considerable number of direct dyes at three salt concentrations. From their figures it is possible to calculate the amount of dye absorbed at any given time. These results are given in Table V for Durazol Blue 2GN for a dyeing time of 3·3 sec. (to compare with the same padding time in the present experiments).

TABLE V

Comparison between Rates of Dyeing and Padding

(Durazol Blue 2GN 200 in 5 : 1 liquor ratio at 90°c.)

(Durazol Blue 2GNP padded with 70% pick-up at 60°c.)

Source	Dyeing Data	Salt Concn. (g./litre) 0	2	6
Lemin *et al.*[2]	Time of half-dyeing, sec.	60	24	12
	Exhaustion at equilibrium, % ...	82	92	94
	Exhaustion after 3·3 sec., %	4·3	10·2	20·4
Present work (60°c.)	Excess dye absorbed during padding, % ...	12	—	60

Considering the first 3 sec. of dyeing as a padding operation, the absorption of dye in excess of the mechanically held liquor is 4% and 20% in the

absence of salt and with 6 g. salt per litre respectively. This is to be compared with the 12% and 60% excess absorption obtained in the present experiments under similar conditions of salt concentration. The effect of 6 g. of salt per litre in both cases is to increase the absorption fivefold. While further detailed comparison is not possible because of the difference in temperature, dye concentration, liquor ratio, and fabric construction, it is very encouraging to note that the two apparently different operations give results of the same order of magnitude.

USES AND LIMITATIONS

Throughout this paper affinity effects have been discussed solely with respect to ending, and it has been shown how this can be minimised either by reducing the magnitude of the depth change and the length of cloth over which it is operative or by dilution of the padding liquor so as to eliminate the initial "tailing". The affinity of the dye during padding has other aspects, too; for example, poor penetration may be obtained owing to the dye being removed from the liquor before it has reached the centre of the fabric. Steps taken in overcoming these disadvantages in padding, although important, must be considered in relation to the overall dyeing process. Thus, from the present point of view, it is desirable to have the padding time as short as possible and the volume of the trough as small as possible, but this may lead to inadequate wetting of the material and shade changes due to small differences in the prepare of consecutive pieces. Similarly, a slack squeeze designed to reduce the value of x will also reduce the penetration in tightly spun or closely woven material. The effect of the cure may then be worse than the malady. The satisfactory running of continuous dyeing processes depends on a proper compromise between all the different aspects, and this in turn is based ultimately on an intimate quantitative knowledge of each step in the process.

Conclusions

While much of what has been discussed is already known qualitatively to the dyer, the present treatment gives a rational basis for quantitatively examining "tailing" in padding and dyeing operations. It has been shown that the extent of the tailing can be expressed by an "affinity factor" x, and that, while this is not a unique property of the dye, it describes quantitatively the differences between dyes under a similar set of conditions and so enables the pad liquor to be diluted to the correct degree to ensure a uniform depth from the start of the run.

The volume of the pad trough is a crucial factor in determining the extent of tailing, and when the liquor content has been changed twice it may be considered that further colour changes due to this cause will be negligible. This gives a method of calculating the amount of cloth used before it runs true to shade.

Now that this theoretical basis has been established, it is hoped to examine many of these problems, so that the best conditions can be worked out to give the least possible change in colour from the beginning of the run and a correct forecast of the dyeing recipe for a given match.

* * *

The author has great pleasure in expressing his thanks to R. W. Speke for suggesting this problem and his encouragement throughout the experimental work.

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IMPERIAL CHEMICAL INDUSTRIES LTD.
DYESTUFFS DIVISION
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(*MS. received 6th May 1954*)

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[1] Vickerstaff, *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954), p. 274.
[2] Lemin, Vickers, and Vickerstaff, J.S.D.C., **62**, 132 (1946).
[3] Speke, *ibid.*, **70**, 221 (June 1954).
[4] J. F. Harris. *Unpublished.*

Discussion

Mr. K. LOWIT: A German firm constructed twenty-five years ago a padding mangle for continuous dyeing with a minute dye box. The levelness of expression was unsatisfactory.

Mr. MARSHALL: The importance of pad troughs of small capacity has been realised for many years, but there appears to have been little attempt made to put this on a quantitative basis and show the relative importance in a variety of circumstances and with various dyes.

Mr. K. A. STOTT: Would the problem of obtaining the minimum size of dyebath be solved, in theory at least, by spraying the dye solution on to the fabric, afterwards applying mechanical pressure to secure penetration?

Mr. MARSHALL: Although the ideal of applying just the correct amount of dye would be achieved by this method, as there is no excess liquid to squeeze out, I do not think that penetration would be obtained in the padding mangle. Apart from this theoretical difficulty, there is the extremely great practical problem of obtaining a uniform spray on both sides of the fabric.

Mr. B. TAYLOR: Mr. Marshall's paper has referred to the padding of dry fabric. Will he explain what takes place when a double pad system is used, especially with non-substantive dyes, i.e. the pigment-pad system? With this system would a greater quantity of fabric have to be processed before equilibrium is reached, or would the variation in shade be within tolerance limits?

Mr. MARSHALL: This question raises an important point. In the repadding of wet fabrics, the actual amount of liquor taken up is the "pick-up difference"; e.g. for a fabric containing 60% liquor before padding and a final pick-up of 80%, the true pick-up in the second padding is 20%, and this is the figure which would determine the yardage for a given value of tv/V. Therefore a longer time is taken to reach equilibrium in the repadding of wet fabrics. In addition to this, there is an interchange effect, the pigment pad bleeding into the chemical pad, and the chemicals in the second pad liquor being diluted by the wet fabric in the case of the system mentioned.

The extent to which this may occur has been investigated and is fully described by R. W. Speke[3]. The quantitative effect of the interchange can be studied by substituting the ratio—

$$\frac{\text{True pick-up}}{\text{Pick-up difference}}$$

for the affinity factor in the present treatment.

Mr. H. A. TURNER: In considering so very clearly the factors which act progressively to influence the concentration of dye in the box of the pad mangle, might not Mr. Marshall have gone one step further and have shown that the real solution of most of the difficulties is essentially mechanical? It lies in avoiding the conditions of slop-padding, where some excess of dye liquor is present on the cloth for a longer or shorter time before it is removed at the nip, and turning to a furnishing system where a volume of liquor not greater than the cloth can absorb is presented from a surface at which no dye adsorption is possible. If any removal of excess liquor is required here, it is done at a stage before dyeing can occur. A synthesis of mangle and printing machine seems to be called for.

Mr. MARSHALL: I heartily agree with Mr. Turner in his remarks concerning the difficulties being essentially mechanical. Indeed, if the mechanical difficulties could be solved along the lines Mr. Turner suggests, it would be possible to employ the ideal continuous dyeing method and apply, say, vat dye pigment and simultaneously the correct amount of reducing liquor.

Mr. M. J. TOPHAM: In reply to Mr. Turner's suggestion that an engraved bowl should be used to avoid tailing, I would like to point out that the method is one-sided and unsuitable for substantive dyes.

Mr. MARSHALL: While a single engraved bowl would undoubtedly lead to a one-sided effect, it might well prove practicable to apply the liquor by this means to both sides.

Mr. G. S. J. WHITE: There appears to be a flattening of the theoretical curves for x at tv/V (Fig. 1). Could the best dimensions for the trough, the rate of feed, or the time be determined from this formula?

Mr. MARSHALL: The flattening of the curve signifies the end of the tailing, and from the value of tv/V and the tolerance in depth that is acceptable, the best value for the trough capacity can be calculated. This value is, however, subject to other practical considerations. From the formula, the smaller the trough the more quickly the flat portion of the curve is reached; but the dimensions must be sufficient to ensure thorough wetting of the cloth. Similarly, if the running speed is increased, thereby achieving a desirable decrease in the affinity factor x, it may be found necessary to increase the trough dimensions, too, so that the cloth can be thoroughly impregnated.

Mr. H. B. MANN*: I would like to support Mr. Marshall's observation that no preferential absorption of water relative to dye occurred in his experiments. This is to be expected under the conditions of impregnation he used (ca. 3·5 sec. immersion at 60°C.), and is in agreement with our own limited data obtained at this temperature with viscose rayon.

The fact that preferential absorption of either dye or water by viscose rayon can occur under the appropriate conditions is, however, clearly demonstrated by the accompanying Fig. 8. The full lines were obtained with the aid of Marshall's equation and refer to a series of values of the substantivity factor x. The broken lines are experimental results obtained in the Textile Research Laboratory of Courtaulds Ltd. at Bocking (Essex) by a centrifuge technique at 25°C. All symbols are the same as those used by Marshall.

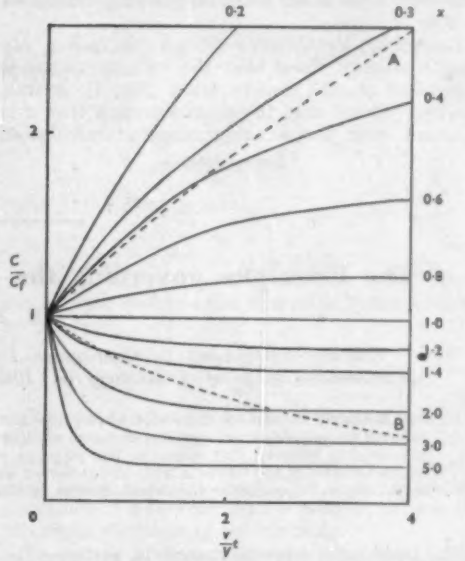

FIG. 8—Effect of Preferential Absorption of Dye or Water on Dyebath Concentration

In Curve A (Fig. 8) the substantivity factor x was initially 0·45. This value was obtained using a coarse yarn (6 denier per filament), a slow-dyeing dye (Sky Blue FF), and an impregnation time of ca. 20 sec.; whereas in order to attain an initial value of $x = 1{\cdot}33$ in Curve B a fine yarn was used (2 denier per filament), a rapid-dyeing dye (Violet R), and an impregnation time of $2\frac{1}{2}$ min.

The deviations from the appropriate theoretical curves arise from the lack of constancy of the parameter x as the dyebath concentration changes, relatively more dye being absorbed from dilute than from concentrated solutions. This is in agreement with previous observations. Thus it must be concluded that—(*a*) preferential absorption of either dye or water may occur during padding depending upon the conditions used; and (*b*) owing to the variations of the substantivity factor x with dye concentration, the theoretical curves may be followed only very roughly in practice.

* Communicated

Mr. MARSHALL*: In fact it will be observed that even in my experiments Durazol Blue 2GNP showed negligible preferential absorption on viscose rayon, and was therefore approaching the conditions under which there is preferential absorption of water. The pore size of viscose rayon is recognised as being smaller than that of cotton, and its molecular sieve action is therefore more pronounced. One would thus expect viscose rayon to show a preferential absorption of water to a greater extent than cotton; the practical significance of this is shown in the reduced ending with viscose rayon piece goods. It is, however, interesting to note that in recent experiments in the Dyehouse Laboratories at Blackley[4] preferential absorption of water on cotton has been noted with Durazol Blue 8GS even under practical padding conditions at 50°C.

Regarding Mr. Mann's second conclusion, my results already show that the affinity factor is dependent on the concentration (Fig. 7); it was, however, found that the approximation that x is constant over the working range of calculation gives curves which closely agree with measurements made under practical conditions of padding. When this approximation is extended to a system that is more akin to dyeing with an impregnation time of 150 sec. (Curve B of Mr. Mann's diagram) and 75% exhaustion of the dyebath, it is not surprising that agreement with the theoretical curve breaks down. In the case of Curve A, where circumstances are rather more closely related to padding, the agreement is very much better. It therefore follows that, while theoretically some deviation from the curves would be expected, practical padding experiments show that this is small. There is thus no confirmation of Mr. Mann's remark that the theoretical curves may be followed only very roughly in practice, except that of his own highly theoretical experiments. I would, however, like to take the opportunity of stressing the importance of Mr. Mann's experiments in analysing the complex nature of the absorption of dyes during padding operations, a complexity which I have in my present paper ignored in order to reveal quantitatively the practical significance of the affinity of dyes during padding.

* Communicated

The Principles governing the Efficiency of a Padding Mangle

H. POTTER

* *One-day Symposium on Continuous Dyeing held by the Manchester Section at the Manchester College of Technology on 19th March 1954, Mr. J. Boulton in the chair*

A simple theoretical discussion shows how the take-up of liquor in a fabric after passing through a squeeze mangle depends upon the distance of closest approach of the bowl surfaces. The mathematical relationship between this distance, the physical characteristics of the mangle, and the compressional characteristics of the fabric is worked out for an ideal case. How the final take-up in any practical case might depend upon other important factors is also considered.

The padding or squeeze mangle is, perhaps, the most familiar and the most universal of all textile-finishing machinery. Basically it appears to be quite a simple machine, which performs its task of removing excess liquid from wet fabric in quite a simple way. But behind this apparent simplicity is such a tangle of variables that their collective quantitative assessment becomes almost a matter of conjecture, and a rigorous mathematical analysis of the process verges on the impossible. Probably for this reason the theoretical aspects of the mangling process have been, as far as can be ascertained, completely neglected, and it is therefore hoped that the simplified treatment presented in this paper will prove to be both interesting and informative.

The physical action of the squeeze mangle in bringing about the desirable removal of liquid from a wet fabric is virtually that of causing the fabric to pass through a narrow gap which firstly diminishes in size and then widens out again. In illustration, Fig. 1 represents a sectional view of a squeeze mangle reduced to its basic essentials of two cylindrical bowls with the fabric between. These bowls, which are not necessarily of the same diameter, rotate with their axes, represented by O and O', parallel. They are evenly pressed together and squeeze the fabric along a narrow circumferential area, whose arc of contact with the fabric is AA'. In the pressure area thus formed, the gap of variable depth is produced by the distribution of pressure as the fabric passes through. In the general case of bowls of compressible material the arc of contact would be flattened in comparison with the rest of the circumference.

Initially the fabric will contain liquid and possibly air spaces trapped in the interstices and, in passing into the pressure area, will gradually decrease in thickness as the pressure increases to a maximum at the point D, where the bowl surfaces are closest together and the fabric thickness a minimum. Up to this point liquid, and possibly air, must be expelled if in excess of the total volume required to fill the available space in the gap over and above that constant part of it which is occupied by the fabric material. After the point D the gap between the bowls will widen and the pressure will decrease; there will be no further expulsion of liquid from the fabric, that left in association with it at D being re-absorbed

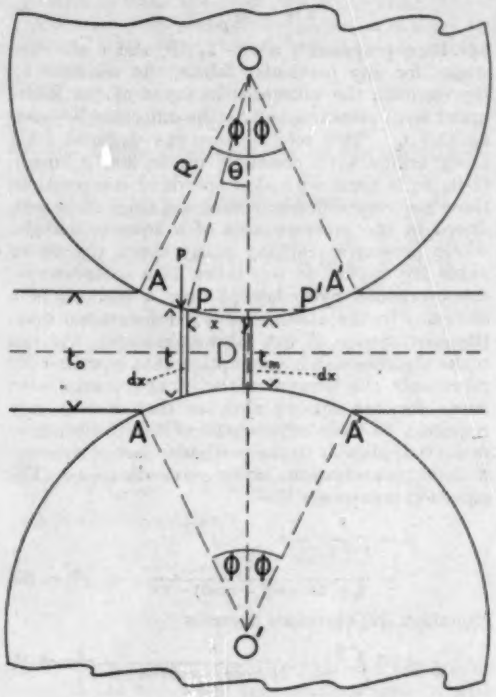

FIG. 1

into the fabric structure by the process of capillarity as the fabric recovers some or all of its original thickness. In other words, the amount of liquid left in association with the fabric after mangling will be that which accompanies it through the narrowest part of the gap between the rollers.

Because there is no means of estimating the amount of air in the fabric at the point of maximum compression, we shall assume that its amount is negligible. For normal mangling processes practical experience supports this assumption, because it is usual to take care to ensure that the fabric is thoroughly wetted-out to the exclusion of air spaces before mangling and also that the remaining air spaces are further eliminated in the "pressure-increasing" stage of the mangling process itself. On this assumption it is easy to find an algebraic expression for the amount of liquid in the fabric after passing through the pressure area.

Let us employ the following symbols—

t_m = Minimum thickness of the fabric, which is also the distance of closest approach of the bowl surfaces

W = Width of the fabric, which is the length of the nip to be considered in the direction of the bowl axes

ρ = Density of the fabric material

σ = Density of the saturating liquid

τ = Weight of liquid left per unit area of fabric after passing through the pressure area

T = "Take-up" of the fabric, which is defined as the weight of liquid left in the fabric expressed as a percentage of the weight of the fabric itself

w = Weight per unit area of fabric

Strictly speaking, w should be the value under the maximum pressure, but we are justified in using the uncompressed value of w on the grounds that, for thin fabrics with restrictions to widthwise and lengthwise extension, the compression is a decrease in thickness only, which will not affect the value of w.

Taking the direction of x as that in which the fabric moves, consider a short length dx at the point of maximum compression D, over which the pressure may be assumed uniform. The weight of the fabric in this length dx of pressure area is $wWdx$ and its volume is $wWdx/\rho$. The volume of liquid left in length dx of fabric after passing through the pressure area is the total volume bounded by the sides of length W, dx, and t_m less the actual volume occupied by the material of the fabric. Thus—

$$\frac{\tau W dx}{\sigma} = t_m W dx - \frac{w W dx}{\rho}$$

or—

$$\tau = \left(t_m - \frac{w}{\rho}\right)\sigma$$

Now—

$$T = \frac{\tau}{w} \times 100$$

Substitution for τ gives—

$$T = \frac{t_m - \frac{w}{\rho}}{w}\,\sigma\,100$$

which, with water as the saturating liquid, reduces to—

$$T = \frac{t_m - \frac{w}{\rho}}{w} \times 100 \qquad \text{(i)}$$

Equation (i), which has been deduced with the fewest assumptions, is nevertheless perfectly general, and, in its rather deceptive simplicity, does focus attention upon the most important dimension in a squeeze mangle process, namely the minimum thickness of the fabric t_m.

To obtain a theoretical expression for t_m, and hence for T, in a general case would necessitate the consideration of a multitude of factors upon which t_m might depend, the main ones being the force pressing the bowls together, the dimensions of the bowls, and the compressibility of the bowl material, the compressibility of the liquid-fabric mixture and its air space content, the viscosity of the liquid, and the structure of the fabric and its speed of movement. To take all these factors into account seems to be impossible. We shall therefore, at this stage, streamline the theoretical investigation by simplifying the real problem, and content ourselves later with a general discussion of the significant factors not dealt with in this simple approach.

Let us suppose, then, that the mangle consists of two identical bowls of incompressible material and that the fabric is of perfect compressibility in the sense that it will show no compressional hysteresis, in other words that the relationship between pressure and thickness will be the same in compression and in decompression. Further, the fabric will be treated as an evenly compressible lamina the squeezing of which is being

performed at a rate slow enough to eliminate the necessity for considering the viscosity effects of the liquid. In this ideal case the task becomes one of integrating the forces required to bring about the gradually changing compression of the fabric in the pressure area and equating to the total force pressing the bowls together, which, of course, is the load on the bowls.

Referring again to Fig. 1, consider the compression of the fabric under an area $W\mathrm{d}x$ at the point P within the pressure area a distance x from the line of centres OO'. Let—

- p = Vertical component of the pressure on the fabric at the point P
- 2ϕ = Angle subtended at O and O' by the full arcs of contact AA'
- 2θ = Angle subtended at O and O' by the partial arcs of contact PP'
- L = Total load on the bowls
- R = Radius of curvature of the bowls
- t_0 = Initial thickness of the fabric
- t = Thickness of the fabric at P.

The area of the column of fabric material over which the pressure p acts is given by $\mathrm{d}x$ per unit width of fabric, so that the force compressing this small area of fabric is $p\mathrm{d}x$. The total force of compression per unit width of fabric is therefore given by—

$$\int p\mathrm{d}x$$

the integration being taken along the total arc of contact of the pressure area. Since we have assumed perfect recovery from compression, the pressure distribution will be symmetrical about the line OO', and we can write that the total force of compression on unit width of the fabric in the pressure area is—

$$2\int p\mathrm{d}x$$

the limits now being between $p = 0$ and $p = p_{max}$. We must therefore have—

$$\frac{L}{W} = 2\int_{p=0}^{p=p_{max}} p\mathrm{d}x \qquad \text{(ii)}$$

From the geometry of the fabric–bowl combination we can see that—

$$t = t_0 + 2R(\cos\phi - \cos\theta) \qquad \text{(iii)}$$

and since we know that p is some (as yet unknown) function of t, we can write—

$$p = f(t) = f\{t_0 + 2R(\cos\phi - \cos\theta)\}$$

We know also that where p is a maximum $\theta = 0$; where $p = 0$, $\theta = \phi$; and again that $R\sin\theta = x$; so that $\mathrm{d}x = R\cos\theta.\mathrm{d}\theta$.

Equation (ii) can therefore be written—

$$\frac{L}{W} = 2R\int_0^{\phi} f\{t_0 + 2R(\cos\phi - \cos\theta)\}\cos\theta.\mathrm{d}\theta \qquad \text{(iv)}$$

in which ϕ is now a constant for fixed conditions of compression.

To perform the integration of equation (iv) it is necessary to know the relationship between p and t for liquid–fabric mixtures. For laboratory-conditioned fabrics the relationship—

$$t = t_\infty + \frac{b}{p + c} \qquad \text{(v)}$$

has been proposed[1], where t_∞, b, and c are constants for any particular fabric, the constant t_∞ representing the ultimate thickness of the fabric under large pressures and b/c the difference between t_∞ and t_0. This relationship was deduced from observations with pressures up to 300 g./sq.cm. (2 lb./sq.in.) and with slow speeds of compression; these are very different conditions from those produced in the pressure area of a squeeze mangle, where pressures reaching many times the above value are applied to wet fabric in a compression–decompression cycle lasting only a fraction of a second. In the absence of any information upon the compression of wet fabrics, however, one can make the reasonable assumption that equation (v) represents the general form of the compression curve for wet fabrics also, so that it will only require a suitable adjustment of the constants to make it applicable to the particular case of squeeze-mangle compression under consideration. The equation transposes to—

$$p = \frac{b}{t - t_\infty} - c$$

$$= \frac{b}{t_0 + 2R(\cos\phi - \cos\theta) - t_\infty} - c \qquad \text{from (iii)}$$

Equation (iv) therefore becomes—

$$\frac{L}{W} = 2R\int_0^{\phi}\left\{\frac{b}{t_0 + 2R(\cos\phi - \cos\theta) - t_\infty} - c\right\}\cos\theta.\mathrm{d}\theta$$

from which, if we substitute—

$$k = \frac{t_0 + 2R\cos\phi - t_\infty}{2R}$$

we get—

$$\frac{L}{W} = b\int^{\phi}\left\{\frac{k\mathrm{d}\theta}{k - \cos\theta} - \mathrm{d}\theta\right\} - 2R\int_0^{\phi} c\cos\theta.\mathrm{d}\theta$$

$$= b\int_0^{\phi}\frac{k\mathrm{d}\theta^*}{k - \cos\theta} - b\phi - 2Rc\sin\phi$$

$$= b\,\frac{2k}{\sqrt{k^2-1}}\tan^{-1}\left\{\sqrt{\frac{k+1}{k-1}}\tan\frac{\phi}{2}\right\} - b\phi - 2Rc\sin\phi \qquad \text{(vi)}$$

Equation (vi) can be simplified considerably if we assume that ϕ is small, small enough in fact to substitute without loss of accuracy—

$$\frac{\phi}{2} \text{ for } \tan\frac{\phi}{2}$$

$$\phi \text{ for } \sin\phi$$

$$\left(1 - \frac{\phi^2}{2}\right) \text{ for } \cos\phi$$

These substitutions are accurate enough at least up to $\phi = 15°$, which is far higher than likely values of ϕ. With these approximations—

$$k = \frac{t_0 + 2R - R\phi^2 - t_\infty}{2R}$$

$$k+1 = \frac{t_0 + 4R - R\phi^2 - t_\infty}{2R}$$

$$k-1 = \frac{t_0 - R\phi^2 - t_\infty}{2R}$$

* This integral can be evaluated by the standard substitution $\tan\frac{\theta}{2} = z$.

Bearing in mind the geometry of the arrangement, we can see that $t_0-(R\phi^2+t_\infty)$, which is much less than t_0, must be much less than R for all practical conditions. Hence—

k is very nearly 1

$k+1$ is very nearly 2

and to a close approximation we can see that—

$$\frac{L}{W}=b\sqrt{\frac{4R}{t_0-R\phi^2-t_\infty}}\cdot\tan^{-1}\left\{\sqrt{\frac{4R}{t_0-R\phi^2-t_\infty}}\,\frac{\phi}{2}\right\}-(b+2Rc)\phi \quad \text{(vii)}$$

To substitute for ϕ in terms of t_m we have—

$$t_m=t_0+2R(\cos\phi-1)$$
$$=t_0-R\phi^2$$

as can be seen also from the geometry. Hence—

$$\phi=\sqrt{\frac{t_0-t_m}{R}}$$

Equation (vii) therefore becomes—

$$\frac{L}{W}=b\sqrt{\frac{4R}{t_m-t_\infty}}\cdot\tan^{-1}\sqrt{\frac{t_0-t_m}{t_m-t_\infty}}-(b+2Rc)\sqrt{\frac{t_0-t_m}{R}}$$

which may be written—

$$\frac{L}{W}=b\sqrt{\frac{4R}{t_m-t_\infty}}\left\{\tan^{-1}\sqrt{\frac{t_0-t_m}{t_m-t_\infty}}-\sqrt{\frac{(t_0-t_m)(t_m-t_\infty)}{2R}}-\frac{c}{b}\sqrt{(t_0-t_m)(t_m-t_\infty)}\right\}$$

From the geometry it will be seen that the second term in the bracket is very small compared with the other two, and since—

$$\frac{c}{b}=\frac{1}{t_0-t_\infty}$$

we get—

$$\frac{L}{W}=b\sqrt{\frac{4R}{t_m-t_\infty}}\times\left\{\tan^{-1}\sqrt{\frac{t_0-t_m}{t_m-t_\infty}}-\sqrt{\frac{(t_0-t_m)(t_m-t_\infty}{t_0-t_\infty}}\right\}$$

For squeezing conditions under large loads $t_m\to t_\infty$, which makes the second term in the bracket negligible also, and the equation becomes—

$$\frac{L}{W}=b\sqrt{\frac{4R}{t_m-t_\infty}}\cdot\tan^{-1}\sqrt{\frac{t_0-t_m}{t_m-t_\infty}} \quad \text{(viii)}$$

Remembering that—

$$t_m=\frac{Tw}{100}+\frac{w}{\rho} \quad \text{from (i)}$$

we finally get—

$$\frac{L}{W}=b\sqrt{\frac{4R}{\frac{Tw}{100}+\frac{w}{\rho}-t_\infty}}\cdot\tan^{-1}\sqrt{\frac{t_0-\frac{Tw}{100}-\frac{w}{\rho}}{\frac{Tw}{100}+\frac{w}{\rho}-t_\infty}} \quad \text{(ix)}$$

from which T could be calculated if the values of the constants were known.

The extension of the mathematics to the case of unequal bowls is not much more difficult, but the further extension to bowls of definite elastic characteristics involves considerable complications.

From equation (ix) one can easily draw certain simple qualitative conclusions regarding the characteristics of the mangle. Firstly, what is axiomatic in squeeze mangle practice, that a greater load means less take-up. As can best be seen from equation (viii), this must always be true for liquid–fabric mixtures, since an increase in L requires that t_m shall decrease, which can be seen if one bears in mind that, since t_∞ represents the ultimate smallest thickness of the fabric under infinite pressure, then, as t_m decreases—

$$t_m-t_\infty \text{ tends to } 0$$

and hence—

$$\tan^{-1}\sqrt{\frac{t_0-t_m}{t_m-t_\infty}} \text{ tends to } \frac{\pi}{2}$$

and $$b\sqrt{\frac{4R}{t_m-t_\infty}} \text{ tends to } \infty$$

From the point of view of removal of liquid, one passage through the mangle should be sufficient, but it does not necessarily follow that the highest load possible is the most economic, since it may be that, beyond a certain load, the slight decrease in take-up for further increase in load might not justify the additional power required to drive the mangle.

Secondly, for the same load per unit length of pressure area, bowls of smaller diameter give smaller take-up. This can be most easily seen, perhaps, if one considers what relationship is necessary between the load and the radius of the bowls to produce a constant take-up. With this condition equation (ix) reduces to—

$$\frac{L}{W}=\sqrt{R}\times\text{constant}$$

which indicates that the load required is proportional to the square root of the radius of the bowls. It necessarily follows that, for a given value of the load, bowls of smaller radius will give a smaller value of the take-up, but there is no clue to the quantitative relationship between take-up and bowl radius.

On the basis of equation (viii) one can justify the statement that squeezing off a fabric as a single layer will give a smaller take-up than squeezing off several thicknesses of the fabric simultaneously. For, if we have n thicknesses of fabric passing through the mangle, we can substitute—

nb for b
nt_∞ for t_∞
nt_m for t_m
nt_0 for t_0

and, if it requires a load L_n to produce a specific value of the take-up T as compared with L for a single layer of material, then—

$$\frac{L_n}{W}=nb\sqrt{\frac{4R}{nt_m-nt_\infty}}\tan^{-1}\sqrt{\frac{nt_0-nt_m}{nt_m-nt_\infty}}$$
$$=\sqrt{n}\,\frac{L}{W}$$

or

$$L_n=\sqrt{n}\,L$$

Conversely, for a fixed value of the load L, it must follow that the smaller take-up will result if the fabric is in a single layer. In the similar hypothetical case of two wet fabrics with the same

compressional characteristics, but one being n times thicker than the other, a fixed value of the load will give the smaller take-up with the thinner fabric.

In a similar way, one can also justify squeezing off in rope form as likely to give greater removal of liquid from a fabric than squeezing off in open width, provided that the same total load is available in each case. For, if one assumes that the fabric rope is equivalent to a thickness n times that of the fabric itself and that L_n is the load required to produce in the rope the same take-up as the load L with the fabric in open width, then, for the multilayer rope, whose width shall be called W_n, the same substitutions as for multilayers of fabric can be made in equation (viii), and we find that—

$$\frac{L_n}{W_n} = \sqrt{n}\ \frac{L}{W}$$

In this case, however—

$$W_n = \frac{W}{n}$$

so that—

$$L_n = \frac{L}{\sqrt{n}}$$

that is, to produce a specific take-up in rope form, in this case, requires less load than that to obtain the same take-up with the fabric in open width. Again the converse, that the same total load will remove more liquid if the fabric is in rope form, must also be true. One must bear in mind, of course, that both deductions regarding fabric in multilayer condition are based on the assumption that compression characteristics in bulk will be the same as for a single layer of material, and the edge effect, which will occur in practice when the fabric is in rope form, is ignored.

At this point we might conveniently consider the influence of the inevitable compression, of the material of the bowls itself in the pressure area of the nip. The theoretical complexities to which this effect gives rise have already been indicated, but it is possible to show what the general practical result will be. The flattening of the bowls in the pressure area is an effective increase in radius of curvature, which will be greater for bowls of soft, easily compressible material than for those of hard material. From the theoretical conclusions on the influence of bowl diameter it follows that, for bowls of the same original size, those of the harder material will give the smaller take-up. Indeed, one might sum up the effect of bowl material by saying that a mangle behaves as if it possesses rollers of variable diameter, this always being greater than the actual by an amount depending upon the softness of the bowls, the applied load, and the character of the fabric being compressed.

The most effective way of removing liquid from a liquid–fabric mixture is hence to use hard rollers of the smallest size compatible with the requisite mechanical strength, a point perhaps best demonstrated by the Küsters mangle*, which represents the most recent development in squeeze mangle practice. In this mangle an ingenious method of evenly spreading a large loading force across hard squeezing bowls of small (about 4 in.) diameter eliminates the possibility of any bending distortion of the bowls and, without sacrificing evenness of impregnation, gives take-up values much less than those obtainable with conventional mangles.

The theoretical deductions which have been made constitute about as much information as can be extracted in a general way from equations (viii) and (ix). Quantitative assessment of the effect of the nature of the liquid–fabric mixture upon the total squeezing effect becomes a more individual matter involving specific values of the constants t_0, t_∞, c, and b, but we might shortly consider here what would be the necessary condition to produce the same take-up in different fabrics of the same basic material with the same squeezing conditions pertaining to the mangle. This condition requires that the composition of the liquid–fabric mixture under the maximum pressure in the pressure area shall be identical for all the fabrics concerned, which is the same as saying that all these fabrics shall be compressed to the same maximum density. The practice of describing squeeze mangles as being of so much "expression", in its tacit assumption that the type of fabric is immaterial, probably owes its success as a good approximation to the fact that the densities of a wide range of fabrics of the same material are nearly the same under such maximum pressures as are met with in normal squeeze mangle practice.

We might next consider the practical influence of the factors which have been so far ignored in the ideal squeezing process, and the first of these is the viscosity of the saturating liquid. It might be said with considerable truth that the effect of viscosity is involved in the compressional behaviour of the liquid–fabric mixture and that the true law of compression for wet fabrics, so far unknown, would automatically take viscosity into account, but this is not very satisfactory from a theoretical point of view. In a general way, however, one can see that, since the liquid is squeezed out through the pores in the compressed fabric, it follows that a liquid of lower viscosity should be easier to remove, and hence that the effect of raising the temperature, for example, should be in the direction of smaller take-up. A smaller take-up should also result from a slowing down in the passage of the fabric through the nip. Both these viscosity effects have also been demonstrated in practical experiments[2]. A further possible effect of viscosity, arising from the fact that with a larger area of pressure the liquid has further to travel before removal, might tend to favour smaller bowls, or, more generally, bowls of smaller effective diameter, giving smaller take-up.

The effect of fabric structure is involved by virtue of the dependence upon it of the size and the shape of the pore spaces through which the liquid is squeezed for removal, and it is therefore associated with the effect of viscosity. In the theory which has been presented simplification has been obtained by treating the fabric as an evenly

* Developed by Eduard Küsters, of Krefeld, Germany; made in Great Britain by Messrs. Hunt & Moscrop Ltd. of Middleton Junction, near Manchester.

compressible lamina, but structure is really taken into account in the necessary assumption regarding the law of fabric compression, since this law was deduced from observations on real fabrics, and the true law of compression for wet fabrics would similarly take fabric structure into account. The one possible effect, not thus accounted for, is in the way the wavy fabric surface, due to the yarn-over-yarn structure, could make a corresponding impression upon the bowl surface, a phenomenon which would be, effectively, a partial penetration of the bowl material into the fabric to the exclusion of the saturating liquid. What would be the net practical value of this effect is difficult to estimate, but it is certainly more likely to be appreciable with easily compressible bowls than with hard bowls, and it is the only point in favour of the former for the purpose of liquid removal.

The other point which we have not yet considered is the possibility of the wet fabric still containing air spaces of significant total volume at the point of maximum compression. This is, indeed, the factor most likely to make a mockery of our deductions, the more so if viscous impregnating liquids are involved. Consider, for example, the effect of increasing the load in such a case. The tendency will always be for an increase of load to bring about the removal of more air bubbles if these are present, but it might, in so doing, leave more space available for liquid and hence lead to a greater take-up, liquid having virtually been squeezed into the fabric rather than out of it as expected. This is not a very likely state of affairs, but nevertheless is one which has been observed in practice[2]. Further, increasing speed of fabric through the mangle could not only carry more liquid through but also ensure that more air spaces were carried through too, to give exactly the opposite effect to that predicted with fully saturated fabrics. The effect of increasing the fabric take-up by passing through the padding process several successive times is probably a demonstration of the gradual elimination of air spaces by pressure. Extreme cases of unsaturation of the fabric can very radically alter the expected take-up figure, and the influence of wetting-out agents in the saturating liquid is a well known method of ensuring good absorbency and normal padding.

Considering the number of factors involved in a simple padding mangle process, it is not surprising that unaccountable variabilities sometimes creep in and, other than suggesting that a keen appreciation of the hidden complexities of the process is desirable and that each padding process then demands individual consideration, much practical advice upon the subject cannot be proffered on theoretical grounds, the theoretical conclusions arrived at having admittedly been in the nature of a show of wisdom after the event. Two points stand out, however. These are that hard small-diameter bowls will give the least take-up, whereas softer bowls are of more use where the liquid remaining in the fabric is to be spread evenly. In view of the actual speed of the mangling operation, which takes a small fraction of a second for normal rates of fabric traverse, the squeezing process can hardly have any but a physical effect.

As to the further progress of our knowledge of squeeze mangling, it seems that, from a fundamental point of view, investigations into the behaviour of liquid–fabric mixtures under a rapid cycle of compression and decompression are desirable. Such experiments, difficult though they would be to carry out, would automatically take into account, and could be used to investigate, such influences as viscosity of liquid, fabric structure, and compressional hysteresis, and, with their wider scope for investigation, would be a very useful supplement to experiments that could be conveniently performed with actual squeeze mangles.

* * *

My thanks are due to the Directors of the Bleachers' Association Ltd. for permission to publish this paper, and to Miss Barbara Mayoh for the care and patience lavished on the preparation of the manuscript.

RESEARCH LABORATORIES
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Discussion

Mr. K. A. STOTT: Is not L (equation viii) the total applied load on the bowls and not the pressure on an element of cloth in the nip? For constant compression of the cloth it seems reasonable that the applied load will need to be less when the bowl size is reduced.

Mr. POTTER: It is perfectly true that for a fixed value of the load the maximum pressure in the nip area is greater with smaller bowls, and the converse—that it will require a smaller load with smaller bowls to obtain a fixed value of this maximum pressure, as is required for a fixed value of t_m—is also true. This is what is implied by equation (viii), which correctly shows a direct relationship between the total load on the bowls and the square root of their radius.

Mr. H. W. BEST-GORDON: Figures already published giving results obtained by use of the Küsters pad indicate that a cotton fabric gave a take-up of 38% and a nylon fabric also 38%. How does this observation tie up with the theoretical approach, for t_m in equation (i) would certainly be different in the cases quoted, while the take-up is the same?

Mr. POTTER: I have evidently not emphasised sufficiently that take-up does not depend solely

upon t_m but is related also to the weight per unit area of the fabric w by equation (i). The fact that the two different fabrics mentioned can, under the same conditions of squeezing, be left with the same take-up is merely an indication that exact compensation has been obtained in this specific comparison between t_m, w, and ρ. As stated in the paper, the condition for the same take-up with the same squeezing conditions in different fabrics of the same material is that the density of the fabrics under maximum pressure in the nip area should be the same.

Continuous Ribbon Dyeing

L. J. CLARKE

One-day Symposium on Continuous Dyeing held by the Manchester Section at the Manchester College of Technology on 19th March 1954, Mr. G. S. J. White in the chair

A method for the continuous dyeing of ribbon is described in which uniformity of shade over long runs is attained by introducing feed liquor into the dyebath through fine jets, thus maintaining turbulent conditions and uniformity of composition throughout the bath.

PRACTICAL

Owing to its narrow width, ribbon has a very low money value in relation to length. From a penny to threepence a yard for ½ in. width in the grey state gives some idea of the values involved.

Where manufacturing methods preclude the use of yarn dyeing, the special difficulties which the ribbon dyer has to face are—

(*a*) Ribbon, being sold in 36-yd. pieces, has to be dyed in hank form, and these hanks tend to be clumsy and difficult to dye evenly.

(*b*) The labour cost of putting on a given quantity of dye is very high indeed.

(*c*) The dye vessels commonly used are not large, so that when a quantity such as 36,000 yd. has to be dyed a single colour, the material has to be split into many batches, with resulting colour variation.

(*d*) Owing to the difficulty of manipulation, vat and azoic dyes are not generally used by ribbon dyers.

It is clear, therefore, that a continuous process, in which the ribbon would be carried mechanically through the successive stages of dyeing, would have very great advantages in labour economy and uniformity of result.

In the early stages we realised that two groups of problems would have to be solved. Firstly, there were the purely mechanical ones of handling a number of ends passing through the machine at one time, and it seemed reasonable to work on the idea that twelve ½-in. ribbons would be dyed simultaneously. The difficulties of controlling and guiding twelve ends and allowing for shrinkage during the passage from the machine were all successfully overcome, but since they were of a purely mechanical nature there is no need to elaborate on this aspect of our work.

The second group of problems related more particularly to the dyeing process, and the two major difficulties were the maintenance of a uniform depth of colour throughout a run and the reduction of the actual time of dyeing to such a low value that the fabric could pass through the operative part of the machine at a reasonable speed without using tanks of unreasonable size.

Experiments in which ribbon was passed through a tank of dye liquor convinced us that variation in colour could not be avoided unless continuous "homogenisation" was possible, i.e. unless the composition of the dye liquor could be maintained constant throughout the dye vessel. In order to try and find out what happened when ribbon was passed through a simple dyebath, we made an experiment in reverse. The ribbon was passed rapidly through a strong dye solution at a temperature low enough to make it doubtful whether any dyeing had taken place; the fabric was not mangled, but merely passed through a pair of tension bars to scrape off surplus liquid. The very wet fabric on then passing through water in a photography dish bled freely, and it soon became apparent that a definite pattern of staining was building up. After running the ribbon for some time, the white blotting paper which covered the bottom of the dish was removed and dried to give a good image of the staining pattern which had been observed in the water. It is reasonable to assume that, had the dish been full of dye liquor, the uptake would have been a reverse image of the bleeding off, so that there would have been areas of such exhaustion adjacent to areas of no exhaustion. Even had it been possible to calculate the overall loss of dye in the bath, any replenishment would have had to be correct not only in quantity but also in distribution.

Our search was therefore concentrated on some technique which would combine agitation, replenishment, and uniformity of distribution. The traditional method of agitating a dyebath, namely boiling, did not attract us for a variety of reasons, and so our thoughts were turned towards jets. We felt that, if liquid could be forced through a fine nozzle under high pressure, the nozzle being submerged below the surface of the liquid, interesting effects might be observed.

One of Einstein's interesting investigations dealt with the mathematical problem of a flag fluttering in the breeze, and he was able to show that this

arose from the fact that, when a stream of air impinges on the flag pole, there is no simple division of the stream into two branches but a generation of vortices alternately to the left and to the right of the flag pole, these travelling in roughly parallel lines on either side of the central line. These vortices behave like solid objects, and the flag takes up a position corresponding to the zone of minimum pressure between the two systems of vortices. Thus, when a flag is flying, what happens is that invisible waves of energy pass along either side, thrusting the fabric first to the left and then to the right.

We attempted to reproduce such an effect within a fluid with the aid of a garden syringe and a domestic baking tin filled with water on which tea leaves were floating. Interesting and encouraging results were soon apparent. After a few adjustments of the metal deflector which took the place of the flag pole, we were able to produce well defined turbulence patterns which moved from the body of the liquid in a manner reminiscent of a rolling boil. It was soon observed that these whirlpools would rebound from the sides of the dish in a manner which one would expect of any wavelike motion, and the next stage was to fit baffle plates, which had the effect of confining the motion to a narrow channel. Later we found that we had observed a phenomenon quite well known to physicists, the Kármán vortex street [1].

From these primitive experiments we evolved our idea of a cell in which the replenishment charge of dye liquor would provide, by its own manner of entering the cell, homogeneity and highly turbulent conditions. By great good fortune our desire to confire the turbulence within narrow bounds caused us to make our first cell about 15 in. square and 1 in. thick with a liquor capacity of approx. 2 litres. The fabric was passed through the cell in **U** form by means of a depressor frame which was so designed as to leave the two arms of the **U** unsupported and, we believe, free to flutter in the turbulent liquid in a manner similar to a flag in the breeze.

All this work was empirical, but when the apparatus was fitted up it worked. Uniform conditions were maintained over long periods of time, and when we compared the ribbons which were being dyed side by side we could not detect any difference in colour between those dyed in the outside positions and those from the middle. The fact that ribbon when spindled up after dyeing forms a disc about 6 in. in diameter enables very close comparison to be made between ribbon dyed at the beginning, middle, and end of a run, and it was with considerable pleasure that we made a large-scale test on 72,000 yd. of fabric dyed tea rose pink in a non-stop run of approx. 20 hr. with complete success.

Temperature control is, of course, very important, but has not presented any great difficulty, since we adopted thermostatically controlled gas-heated water jackets for the cells, and we normally run within $\pm$ 2°C. of the desired figure.

Normally we do not completely exhaust our dye liquor, since the rate of pumping creates a small overflow, but the saving of labour and hence of manipulation charges is so substantial that a slight waste of dye is of no economic significance.

The above work was done with direct dyes selected for their rapid rates of strike, and for three years now we have been using this technique to dye large quantities of goods with such dyes. Encouraged by this success, we turned our attention to azoic and vat dyes, and found that without too much difficulty we were able to produce very level results. Broadly speaking, the technique employed with these dyes is to run the fabric through a simple padding mangle followed by an air dryer, the impregnated and dried fabric then passing through the cell in which the developing liquor appropriate to the dye used is applied by our standard turbulent method. The fabric passes straight from the developing cell into a cold water wash cell, where again highly turbulent water removes surplus chemicals, and so on through a soaping-off tank kept at a full rolling boil.

Neither levelling agents nor salt appear to be of benefit in our process, and this may be due to their aggregating effect on direct dyes [2], which would slow down the movement of the dyes.

THEORETICAL

After our process had been evolved, we found that our views received support from those of Vickerstaff [3]. The work we have done tends to show that purely mechanical factors, such as rate of liquor flow and turbulence, deserve as serious attention as the diffusion of dyes within fibres. Powerful forces are at work causing particles of liquid to adhere strongly to solid surfaces, and unless turbulence is high, particles of liquid which have discharged their dye content may tend to linger at the fibre surface and prevent the approach of fresh dye liquor.

The surprising absence of "tailing" in our process may be explained by the high rate of feed and the small volume of the dyebath [4]. Where very large tanks are used the mechanical problems of mixing a replenishment charge uniformly throughout the liquor are clearly very serious, but with small volume and high turbulence, where the new charge acts as the mixing mechanism, homogeneous dye liquor is easily obtained.

One interesting aspect of our work has been the possibility of using mixtures of dyes of widely different rates of dyeing. The use of slow and rapid dyes together causes no embarrassment owing to the very short time of immersion: all that is necessary is to increase the proportion of the slower dye to compensate for the lack of balance.

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(*MS. received 4th April 1954*)

References

[1] See e.g. Prandtl, L., *Essentials of Fluid Dynamics* (London: Blackie & Son Ltd. 1952), p. 183.

[2] Vickerstaff, T., *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954), pp. 70–75.

[3] Idem, *op. cit.*, pp. 144–162.

[4] Cf. Marshall, W. J., J.S.D.C., 71, 13 (Jan. 1955).

Discussion

Mr. E. BUTTERWORTH: How does the fastness to rubbing and washing obtained by the method described compare with that of the same dyes dyed by the normal method?

Mr. CLARKE: Fabrics dyed by the continuous process have been tested by the S.D.C.'s severest standards and have proved fully equal in fastness, both to rubbing and to washing, to those dyed by any other process.

Mr. B. KRAMRISCH: In Mr. Clarke's paper, reference has been made solely to the dyeing of viscose rayon. As nylon and Terylene ribbons are likely to be required for use on garments made from these fibres, can the continuous dyeing apparatus described be used for narrow fabrics of nylon and Terylene? Is the great turbulence created sufficient to allow the production of full shades of disperse dyes on Terylene without the use of carriers?

Mr. CLARKE: So far the only work done on nylon has been in lingerie shades, which have been dyed satisfactorily.

In the case of Terylene no work has yet been done, but there is every reason to think that high turbulence would be of great assistance, although it is doubtful whether the very short dyeing times obtained on viscose rayon and cotton would be practicable with such a difficult fibre.

Mr. P. A. SENN: Is it possible to match any shade, including medium and dark?

Mr. CLARKE: Although most of the commercial development has been with light shades, no difficulty has been experienced in producing heavy shades giving good colour matching.

Mr. J. F. D. BUTTERWORTH: Is the lecturer interested in the intensifying of turbulence by the use of ultrasonic excitation in his dyeing cell?

Mr. CLARKE: The published accounts so far available on ultrasonic excitation are rather meagre, but they tend to indicate that the energy per unit area has to be so high as to render cost a very serious item. No experimental work has been done in this field.

Mr. H. POTTER: In view of the fact that ultrasonic energy can be successfully used to remove small particles of dirt from fabrics, would it not have the effect of preventing dyeing rather than assisting it?

Mr. CLARKE: This is a very interesting question, but until some work is done on it one can only speculate. My own feeling is that ultrasonic vibrations would merely cause the particles to oscillate, giving a sort of push–pull effect of small amplitude. Turbulence is accompanied by large movements of a circulatory type, causing free movement within the dye liquor.

Explanatory Papers on Modern Theory

Foreword

It has become obvious in recent years that many members of the Society have found difficulty in understanding some of the papers published in the *Journal*. This is to be expected, perhaps, since the pace of scientific investigation has accelerated, and for older members the gap between what was learnt in student days and what is demanded of students of today is almost frightening.

It is certain, however, that everyone concerned with the practice of dyeing would benefit by an understanding of modern theories. Therefore, at the request of the Council, the Publications Committee has devoted considerable thought to how this very difficult problem could best be tackled. The Committee has decided to publish a series of papers which will summarise, as simply as is possible, scientific advances which are of interest to practical dyers. It should be made clear that some of the reading will not be too easy and will call for effort from the reader, but an understanding of these papers should go a long way towards ensuring that reading of the more scientific lectures and communications in the future will become easier and more worth while.

In Part I of the first paper, which appears below, Mr. H. A. Turner discusses in detail this problem of the difficulty of understanding theoretical papers, and then gives a general account of dyeing theory; Part II will deal with dyeing processes in action. Later, it is intended to publish contributions from Dr. L. Peters and Mr. J. S. Ward.

If this series of papers meets with approval, the Committee will consider an extension to other scientific topics of interest to members. Comments from members would be most welcome.

The Publications Committee is grateful to the contributors to this series, who have attempted a most difficult task. They have devoted much time to their efforts to effect a closer understanding between theory and practice, and if this object be achieved, it will surely be for the general benefit of the technology of coloration and in accord with the objects of the Society.

JOHN BARRITT
Chairman
Publications Committee

Theories of Dyeing

I—Dyeing Processes at Completion

H. A. TURNER

> But Scientists who ought to know,
> Assure us that they must be so,
> Oh! let us never, never doubt
> What nobody is sure about.
>
> BELLOC

THEORY AND PRACTICE

During the past thirty years or so, the contents of the *Journal* have changed a good deal both in manner and in matter. The period has been dominated by the rise of exact fibre-chemistry and by the increasing importance of the man-made fibres. It would not be far from the truth to say that most of the significant modern developments in both dyeing and printing have sprung from these two groups of subjects. Perhaps the greatest developments have come from the challenge of the manufactured fibres. They made it possible to eliminate the bad or irrelevant properties of the traditional fibres and to introduce favourable ones in useful proportions. But knowledge was incomplete, and progress was not continuous, so that it has often been found that, when fibres are planned to give better mechanical properties, they become more difficult to dye by the methods available. Nevertheless, with fibres whose shape, internal arrangements, and chemical properties are coming under deliberate control, it is natural, and indeed inevitable, that there should be a desire to know more of the mechanism of dyeing processes, so that they, too, can be manipulated with more certainty and in a greater number of ways.

Thus, there has been a second wave of theoretical advance in the history of the technology of coloration, a history which is coincident with the history of modern science. The first wave concerned the principal agents, viz. the dyes. Complex organic molecules were synthesised in great variety, by processes of inspired cookery, and the introduction of each of these products into the dyeing industry was far more important than their methods of synthesis. Thus, much efficient dyeing could be carried out with little knowledge of dye chemistry. The second wave has been occupied with processes, with dye molecules going into, and out of, more or less well defined fibre structures, with phenomena examined on the move. This picture is, of course, much

neater and more arbitrary than the reality, but it brings one or two important generalisations into sharper definition.

While all this has been going on, the dyer has had to keep on dyeing. He himself made some contributions to theory while the movements were in their early stages. But there is no let-up in industries so basic and so traditional as the textile manufacturing and processing industries, no stopping to clean the slate and start afresh. Operations have to be kept going by inherited and slowly acquired craft experience, and with irregular injections of novelty, improvement, and system. To keep these operations going is, for many, a full day's work, requiring undivided attention. Who is going to design new dyes and auxiliaries, construct new fibres, and, in general, investigate more narrowly the processes of manufacture in all fields?

In the necessary division of labour, much has been taken over by the scientist, both pure and applied, and it has, on the whole, been a very convenient and fruitful arrangement. It has come to be accepted as the normal order of things, so that separate branches of the chemical industry have been entrusted first with the discovery, and then with the provision, of dyes, chemicals, and fibres. For the successful exploitation of these materials, the producers have had to supply the users with a great deal of information about the manner in which they can be most efficiently handled. There has thus been a greater concentration of scientific workers in the dyemaking and fibre-making industries than in the user industries. This disparity still exists, although it is not now so great as it was a few years ago. It may seem to be exaggerated because, in the present industrial system, it is an essential part of the policy of the chemical firms to disseminate information about their products and the processes for which they are used. The user firms, supplying non-technical customers and faced with a different kind of competition, need to be more careful about disclosure; or rather, less of their technical information is available for publication. The textile manufacturing and processing industries are, of course, as interested as any others in long-range investigation, and have delegated much of it to the research associations; but they do not always encourage within their own ranks a sufficient number of people trained to take over from these associations at the appropriate stage. All industries depend upon the universities for fundamental discovery and for the preliminary training of their scientific staffs. Here, the applied science departments which affect the dyemaking and dye-using industries directly, while important, do not represent a very large proportion of the total scientific manpower in operation.

As these activities have extended in range and increased in volume, it is inevitable that there should be a reflection in the pages of the *Journal*. Since, on the whole, the scientific worker has had more time allotted to him for investigation, and greater freedom to publish accounts of his results, ideas, and speculations, the idiom has tended to change, and the technical articles of former issues are acquiring a more scientific flavour. Members of the Society whose main work is in production find that this idiom tends to grow less and less familiar. It has been represented, with some justice and with growing insistence, that these members are not finding a sufficiently intelligible message in the lectures given and the papers published. How may this be put right?

It should first be made clear that this situation is a sign of the times and does not apply to the textile industries alone. Chemistry itself has changed greatly in the past few decades, so that those who might properly claim to be good chemists twenty or thirty years ago find it difficult to keep abreast of the subject. Modern chemistry is less concerned with completed events than with the quantitative study of change, from instant to instant. This study is intrinsically difficult, and the results require prolonged and careful attention before they can be understood. It may still be possible to state the broad principles in simple terms, but this becomes harder when detailed application of these principles is contemplated. A common technical operation, something that is an ordinary everyday event in the dyehouse or bleachcroft, generally turns out to be very complicated when it is broken down into its component factors for scientific investigation. In this field, the properly qualified scientist is in a stronger position than the industrial operator, and this statement may be made without any reflection upon the skill, intelligence, or experience of the latter.

If the scientist is a genuine representative of his kind, and if he is given reasonable facilities for his work, he will be able to do this breaking-down more efficiently, and to draw more effectively on the general body of scientific knowledge for methods and for inspiration, than if he were restricted to technical experience drawn from the narrower field of his industry. It must be realised, however, that when investigation is carried out efficiently, the inherent complexity of the studies will probably make simple exposition very difficult. The scientific worker will also be denied valuable means of communicating his ideas accurately and concisely to his fellows if he is not allowed to use the specialised terminology which has been developed in order to facilitate this kind of description. To say this is not to condone the awkward, inaccurate, or obscure prose in which, even now, scientific and technical contributions of great interest and importance are frequently presented.

The practical man, for whose benefit this scientific work is being conducted, will, for the most part, expect to be given the significant conclusions in a form in which he can apply them, either as a new product or as new working directions. It is not always necessary to appreciate all the steps by which a product or a process has been reached. Few dyers or printers would find it desirable to know all the theoretical organic chemistry or all the technicalities of dyemaking

which go to make one of the dyes that they wish to use. The same may be true of the rapidly developing theories of dyeing and of fibre structure. But these have an immediate connection with the industrial processes of coloration, and it is more natural that the dyer or the printer should wish to know some of the details, and to see how they affect large-scale operations. Whatever may be said of other kinds of scientific knowledge, these theories are neither ideal nor abstract in either inception or development; they are meant for use when they have been properly worked out.

At this stage a warning is necessary. Really thorough and extensive investigation, founded on scientific methods and principles in the form in which we see them today, is a comparatively new thing in industries which have a very long history. No matter how attractive the possibilities of such investigation, it cannot produce sound results in five minutes. Even now, little more than the foundations of the system have been laid, and so it will often happen that the scientific worker, after much work and thought, will do no more than restate, perhaps in a rather different form, conclusions that have long been known in industrial practice. This is not to be taken as evidence of redundant effort. If the conclusions are stated in quantitative form and are connected with general principles, they are much more likely to be constructive and to lead to developments which works experience alone could not supply.

For these reasons, all members of the Society should see that no limitation is imposed on any scientific worker who wishes to use the resources of the Society to communicate his work, if the expert advisers of the Society say that it is valuable. The most lucid and direct method of presentation should always be sought, but in some subjects and with some kinds of treatment the appeal can never be very wide. It seems, therefore, that there is a need for the simple exposition of the principles upon which some scientific investigations are based and of their implications. Of work which interests the dyer directly, none is likely to have a greater appeal than that which seeks to make clear the intimate details of the common dyeing processes.

THE SCOPE OF DYEING THEORY

Among substantive dyeing processes, with the dye in a stable soluble form, much progress has been made in constructing detailed, self-consistent theories of the manner in which dye from the dye-bath enters the fibre and is retained there. As these things go, progress has been rapid, because dyeing processes of this kind are special examples of a more general group of phenomena, in which substances are absorbed from solution by solid bodies. There is thus a large amount of analogous data on which has been constructed a considerable body of theory in physics and physical chemistry, and this can be applied to the specific problems of dyeing. Some dyeing systems may be difficult to investigate, or the results may be difficult to interpret, because both the fibres and the dyes in them are complex substances. The experimental problems which arise from the need to use pure and uniform materials, and from the necessity of defining the working conditions precisely, may be very great. On the other hand, because dyes are coloured substances, and because there are fairly simple laws connecting the absorption of light by their solutions with the concentration, it is often easier to measure the movement of dye in a system than to measure the movement of chemically simpler substances.

There has been a tendency to separate, for the sake of convenience, the total phenomena in the dyeing process into two groups. One includes the dynamic aspects, determined by the rules which govern the rate at which dye passes between the bath and the fibre, the rate at which it diffuses from the rim to the centre when it is in the fibre, and the extent to which these happenings are influenced by the separate conditions of the operation, such as temperature, concentration of the bath, pH, concentration of added electrolyte, and so on. The other group is concerned with those factors which cause retention of dye in the fibre once it has arrived there, factors which have long been known by the inclusive term *affinity*. The latter factors are at work, of course, during the whole process of dyeing, but they are most conveniently investigated when the process has come to a standstill, i.e. when it has reached equilibrium. Here, generally speaking, the maximum amount of dye has been taken up under the conditions of the experiment. For this reason, affinity measurements are made when the dyeing system appears static or quiescent to the observer, though the individual molecules are far from static. Because affinity, that is to say the affinity as defined by the physical chemist, is, of the two classes of phenomena, rather easier to explain in simple terms, it will now be discussed.

AFFINITY

When any kind of matter is in a state—liquid, gaseous, or in solution—in which its molecules are reasonably free to move independently, it will always tend to distribute itself uniformly throughout all the space which is accessible to it. This is because the movement of the particles is generally at random, and there is no reason for them to stay more in one part of the space than another. If they are in a crowded state, and more space becomes available to them, they will spread into it spontaneously. If, however, they are required to be concentrated from a large volume into a smaller one, some deliberate external intervention is required. This is one aspect of the universal Second Law of Thermodynamics. The physicist and the physical chemist often find thermodynamics very useful in studying problems of diffusion or concentration—spreading or crowding—of molecules. For one thing, it generally takes the simplest possible view of the occurrence, because it is concerned only with the initial and the final states of a system which has changed in some way, and neglects most of the intermediate stages in the

path of this change. It is thus a potent agent for bringing ideas to earth, and treating different systems on a common footing, for the starting-point of the change can be made a standard one, something which is, perhaps, never realised in practice, but which can be readily imagined.

Now, the dyeing of a fibre with substantive dyes seems to be a departure from the spreading-out principle. A very dilute solution of an acid dye, along with an acid, is used for dyeing wool, and, in a short time, nine-tenths of the dye has left the large volume of the bath and is found crowded into the very much smaller volume of the fibre. Some new influence has intervened, and has made the random movement of the molecules more purposeful, so that they now stay in one part of the dyeing system. This behaviour was always something of a mystery when the chemists had only a simple and relatively inelastic system of valency to define the forces operating between one atom and another, which led to the concept of saturated molecules with no valency to spare after the atoms in them had been joined together. The greatest advances in chemical theory have come from the recognition that there is a great variety in the combining forces inherent in an atom, so that, even if it is combined in a molecule, it may still have some valency left to attract atoms in other molecules, and thus to link the molecules themselves together. These "spare valencies" are often very active in linking molecules of dyes to the molecular structure of fibres, so restricting their natural tendency to wander out of the fibre once they have got into it. Thus, during dyeing, more and more dye molecules find themselves attached to the fibre by this means. The stronger the attachment, other things being equal, the more denuded becomes the dyebath, the natural spacious home of the dye, and the greater is the affinity. It should not be thought that the dye molecules submit to capture by the fibre without a struggle. They oscillate, rotate, take up new shapes from moment to moment, and are also bombarded by water molecules which have followed them from the bath into the fibre. The higher the temperature, the greater will be this movement, so that, in fact, some do wrench themselves free. This is why exhaustion is never complete and fastness to washing is never absolute. The stronger the attachment, i.e. the more powerful the individual spare valency forces or the greater the number of them that bind the dye molecule to the fibre, the fewer molecules will get free once they have become attached. This agrees with the empirical conclusion that there are degrees in the affinity of dyes for a fibre.

Now the dyer has always measured affinity by the proportion of dye taken up from the bath, and, in effect, the physical chemist also has recognised this criterion. It does not follow that the strength of the attachment between dye and fibre due to the partial valency forces is immediately reflected by exhaustion of the bath. These forces may be given different jobs to do. If dyeing occurs from a very dilute bath, the collection of the dye into the fibre is much more difficult: the dye has to be "compressed" more than if the dyeing takes place from a stronger bath, or, even more markedly, from a print during steaming. On the other hand, if a pale shade is being dyed, there are more places within the fibre where any single unwary dye molecule can be trapped. We shall discuss later the effects of addition of salt, etc., but already it will be seen that there are many factors which can cause a difference in the absolute or the proportional uptake of a given dye by a given fibre and so can alter the affinity. Through all this the intrinsic attraction between the dye and the fibre should remain approximately the same. The chemical constitution of the fibre substance is almost the same in, say, viscose rayon as it is in cotton, so that it might be expected that the strength of attachment of the molecules of a given direct dye to the cellulose would be pretty much the same for each fibre. Nevertheless, when dyed under identical conditions, the viscose rayon will take up more dye than the cotton, and this is, of course, ascribed to differences in arrangement of the molecules of the fibre and not to differences in constitution. Although, from the point of view of practical application, it would be useful to have a measure of the affinity of a dye for a fibre in any of the changing circumstances of use, it is more informative if the affinity is expressed in such terms as give a measure of the strength of chemical attachment between dye and fibre.

ENERGY IN DYEING

One of the ways in which the relative strengths of a number of magnets could be assessed would be to find out the force which would be required to pull each of them from the same piece of soft iron, or, rather better, to find out how much work would be required to move any specified magnet right out of the range of attraction. This is what is done in determining the strength of attraction between a dye molecule and the fibre-substance. The answer is given in units of work or energy, and since, normally, the energy which is furnished when the dye and fibre come together, or which has to be put in to separate them, is in the form of heat, the strength of attachment is usually expressed in terms of the heat exchange for a given amount of dyeing. Of course, it is quite impossible to make these measurements on a single molecule of dye, for, apart from the difficulty of manipulating anything so small, the dye molecules in the dye bath are on the move, and as they are all moving with different speeds, the one we chose to consider might be moving too fast to be stopped by the pull of the fibre. All our results must represent the average behaviour of a very large number of molecules.

When, in imagination, we try to find how hard it is to pull a "dyed" dye molecule from the fibre, this operation has to be done in a special way. The dye molecule has to be moved out of range of the fibre with extreme slowness, otherwise we shall do more work than is necessary, and some will be expended, not in performing the simple separation, but in doing things in which we are not immediately

interested, such as heating up the solution. The methods of thermodynamics have been devised for carrying out operations in imagination in this ideal fashion, and this is the technique of reasoning that is now used. We have seen that the process of removing a dye molecule out of the range of the force which attaches it to the fibre—stripping it, in fact—means that work has to be done. It follows that when the reverse process of dyeing takes place, and the dye molecule is pulled to the fibre by the partial valency forces, some energy is given out and can be available for a variety of purposes. The early stage of stripping a molecule is like pulling back a weight attached to a length of elastic, the other end of the elastic being anchored. *We* have to do the work. When the stretched elastic is released (the dyeing process), *it* does the work. But, as we have seen, dyeing has another consequence into which calculations of work enter. The dye leaves its spread-out condition in the solution and is crowded into the fibre. Work has to be done in bringing it into the more compact form, just as work has to be done in compressing 100 litres of air into 1 litre. If we do this compression extremely slowly, we can calculate the bare amount of work required for the purpose. Thus, with certain qualifications, we can say that, in dyeing, work which is furnished from the pulling-in of the dye molecules by the fibre is available for collecting them from their spread-out state within the dyebath into their crowded state within the fibre. Let us imagine that we are carrying out an actual dyeing and are within a hair's-breadth of reaching the equilibrium condition when the process will stop. To put the last little parcel of dye in, we shall, in effect, have to compress it from the concentration at which it exists in the dyebath (equilibrium dyebath concentration) and bring it to the concentration at which it will exist in the fibre (equilibrium fibre concentration), and this will require a certain minimum quantity of work to be done. When this dye gets into the fibre, it will be attracted by the partial valency forces, and the process will furnish a small amount of work. Since the dyeing process then stops, we know that the work furnished by the attraction has been just sufficient to cause the compression and no more. If we can calculate the work required to bring the small parcel of dye from equilibrium dyebath concentration to equilibrium fibre concentration, we know how much work is furnished in the actual attachment of the dye molecule to the fibre, and hence we have a measure of the strength of this attachment, the intrinsic affinity of the dye for the fibre.

To make this quite clear, let us consider two direct dyes, each dyed on the same weight of viscose rayon at the same temperature and from a dyebath of the same volume at the same initial concentration, until, for each, equilibrium is reached. With dye A, we find that 70% of dye is taken up by the fibre and the remaining 30% remains in the bath. The corresponding figures for dye B are, perhaps, 40% and 60%. It is obvious that the last small parcel of dye A which is introduced to consummate equilibrium will come from a more attenuated dyebath, and will go into a more crowded fibre than will the corresponding parcel of B. Since it does go into the fibre, it follows that the attraction of the fibre for A will be greater than the attraction for B, and, on the above definition, the affinity will be greater also.

Having got so far, we may now be able to give an idea of how the calculations are made, and to introduce some of the symbols which are encountered in communications dealing with the subject, symbols which hitherto may have caused some mystification. It has been shown that the essentials of the calculation consist in determining the minimum amount of work which must be expended to bring a certain small quantity of dye, against its natural tendency to occupy the greatest amount of space available, from the concentration which rules in the dyebath to the concentration which rules in the fibre. Obviously the experimental determinations on which this calculation will be based are the concentration, or degree of crowding, of dye in the dyebath at equilibrium, and the corresponding equilibrium concentration of dye in the fibre. By carrying out carefully controlled laboratory experiments which imitate the ordinary dyeing conditions, and then determining the amount of dye in bath and fibre, usually by colorimetry—although certain chemical methods may be available—it is generally easy to get the data. Sometimes, as for example when wool is dyed with certain acid dyes, equilibrium is reached very slowly and there is some danger of decomposition in the fibre. Then a rather more roundabout approach is necessary. In our experimental work we shall not saddle ourselves with more unknown factors than are necessary and so we shall use carefully purified dyes, etc. and carefully selected and purified fibres.

THE CONCEPT OF POTENTIAL

In the calculation, the idea of *chemical potential* is introduced. The concept of potential appears in a number of guises in physics and physical chemistry, and in the most general sense is a quantitative expression of the ability of a specified amount of matter (for this purpose we may have to count electrons as matter) in a given state to do work when it is allowed to go into some other state. The simplest example is a mechanical one. If a pound weight is standing on a solid floor, it can do no work. If it is lifted 10 ft. into the air, someone will have to do 10 ft.-lb. of work. If, suitably harnessed, it is allowed to descend to the floor again, we can, at most, get our ten units of work back. The weight is at zero potential on the floor and at a potential of 10 when it is up in the air. If it is lifted only 5 ft. its potential will then be 5. If it is allowed to descend from the 10 ft. level to the 5 ft. level, it will do a maximum of 5 units of work, and there is said to be a potential difference of 5. In electrical work, the potential of the earth is taken as the starting point or zero, and potentials can be expressed in volts. If we have two terminals, A maintained at a potential of 200 v. above that of the earth, and B at a potential of 100 v., and if

we connect between A and the earth a motor which will take one ampère of current, we shall get from it a continuous output of 200 units of work per second. If another motor, also taking 1 amp., is connected between B and earth, this will furnish only 100 units of work per second. If this same motor is connected between A and B, where the potential difference (or "electromotive force", as the electrical engineer may call it) is 100 v., we shall also get 100 units of work per second. These examples show how the state of analogous systems may be expressed as potentials with reference to some easily defined state, and how the potential difference between two systems defines the work which is transferred when a certain amount of matter, or a certain number of electrons, passes from one to the other. Since a high potential signifies a greater energy content, and a low potential a smaller one, it will be seen from the mechanical example that, if the change is from a lower to a higher potential, there must be outside intervention, i.e. work must be furnished for the change. On the other hand, as in the example of the descending weight, work is given out in passing from a higher to a lower potential, so that, if all obstacles are removed, this is the direction of spontaneous change.

In considering molecules of dye in a dyebath or in a fibre, we have seen how the natural tendency of the molecules is to spread out or dilute themselves into the greatest possible space, and how, if they are to be compressed or crowded into a smaller space, work must be done. If, for instance, a dye solution is placed in the bottom of a glass cylinder and a layer of water is placed carefully on top, in a little while the dye will have diffused into the top layer so that the concentration is the same in top and bottom layers. The spontaneous change has been towards dilution of the original solution. This suggests that the concentration or the crowding of molecules into a space can be represented as a potential. In the example just given, we can say that the dye in the original dye solution was at a relatively high potential, and that the potential of the plain water, because there was no dye in it, could be taken as zero. At the surface which originally separated these two layers, there would be a difference of potential, and under the influence of this difference the dye would begin to migrate from the layer of high to the layer of low potential. When the concentration had become uniform throughout the system, there would be no difference of potential between any one part and any other. In the absence of any reason for dye to be more concentrated in any one part than in the rest, migration within the system would cease.

The potentials we have just been considering are essentially *thermodynamic potentials*. A special form of thermodynamic potential is set up when changes in the system which produce it depend upon a chemical change. In the system which is of greatest interest to us at the present— the dyeing system— the potential of the dye in the fibre is related to the proportion which is present. This proportion is, in turn, determined in part by the chemical attraction which exists between molecules of the dye and those of the fibre, or, to put it in a somewhat different manner, the chemical reaction which takes place between the two on dyeing. A thermodynamic potential which takes cognisance of the chemical factor is therefore known as a *chemical potential*.

In the very simple example, given above, of the distribution of dye between two layers of water, it is seen that the difference of potential between the two layers, a difference which causes the dye to migrate from one layer to another until an equilibrium state is established, is likely to be expressed in some way which brings in the concentration or crowding of dye molecules in the two phases. In the dyeing system, the situation will be rather more complicated. If dye is highly concentrated in a fibre, it ought, given the opportunity, to escape from it into some place where the crowding is less. On this count, the potential in the fibre should be high, higher at any rate than in the place to which it can spontaneously migrate. But, in actual dyeing, there are times when, although dye is still being taken up by the fibre, it is certainly more concentrated in the fibre than it is in the bath. The tendency to migrate engendered by differences in concentration between fibre and bath must therefore be modified by the attraction of the fibre, and of the solvent also, for dye molecules. This example shows how the concentration of dye in the fibre will tend to increase its potential in that phase, while the attraction for the fibre will tend to diminish it, since, as we have seen, the dye must always tend to move from a region of high to a region of low potential.

CALCULATION OF AFFINITY

We are now ready to look at the form of calculations actually employed. Each phase, dye and fibre, is dealt with separately. The chemical potential in the fibre is called μ_f and that in the dyebath μ_s. While dyeing is going on, μ_s must be greater than μ_f; but when equilibrium is reached and the process ceases, μ_s and μ_f must have become equal. It has been seen that the potential of dye in, say, the fibre is determined partly by the concentration and partly by the attraction between dye and fibre. Now, by suitable alteration of the conditions of dyeing, we can make the concentrations of dye at equilibrium in fibre and bath respectively pretty much what we want, while it is to be presumed, because there is no evidence to the contrary, that, for small or moderate concentrations of dye in either phase, the chemical attraction between a given dye and a given fibre substance will have a constant value, a value that we want to find. In order that the potential can be related directly to the chemical attraction without the distraction caused by some unknown share of the concentration values in the effect, it is customary to consider the potential of the system in a standard state, a state which is chosen, admittedly, to facilitate calculation. This standard potential is written μ_f° for the fibre and μ_s° for the bath, and refers, for a given class of

dye and fibre substance, to a standard concentration or, more correctly, a standard value for the crowding of the dye molecules. This value, μ°, for the particular phase will now include the *constant* contribution to the potential made by the chemical attraction plus a *constant* contribution made by the concentration. The greater the difference $\mu_s^\circ - \mu_f^\circ$ between the potentials in the standard condition of the system, the greater the standard measure of the tendency of the dye to go into the fibre from the bath and the greater the value of the affinity, expressed in such a form that one dye can be compared with another.

In our dyeing experiments it may be impossible to realise an equilibrium in which dye is in the standard state in each part of the system, so we have to take the experimental values that we can get and transform them to the standard values. This is done by putting—

$$\mu_f = \mu_f^\circ + (\boldsymbol{R} \times T \times \ln [D]_f) \qquad \text{(i)}$$

where $\ln [D]_f$ is the natural logarithm (to the base "e") of the concentration or actual state of crowding $[D]_f$ of the dye in the fibre, T is the temperature reckoned from absolute zero (−273°c.), and $\boldsymbol{R}$ is a constant value. The last term, $\boldsymbol{RT} \ln [D]_f$, comes in fact by analogy with the calculations of the work required to compress the molecular weight in grams of a gas from a volume it may be occupying to a standard volume, for, by one device or another, dye molecules in the fibre before fixation or in the dyebath are considered to have the freedom of gas molecules and to be susceptible to a similar treatment.

The last term in equation (i) therefore represents the amount of work which must be done to collect or to compress dye from the standard state of crowding corresponding to the potential value μ_f° (at which the crowding is unity, so that $\boldsymbol{RT} \ln [D]_f^\circ$ becomes zero*) to the observed state of crowding corresponding to $[D]_f$. The potential μ_f corresponding to the particular state of crowding is thus the standard potential plus the extra work or, as we have seen—

$$\mu_f = \mu_f^\circ + \boldsymbol{RT} \ln [D]_f \qquad \text{(i)}$$

An exactly similar equation can be written for the dye in the dyebath—

$$\mu_s = \mu_s^\circ + \boldsymbol{RT} \ln [D]_s \qquad \text{(ii)}$$

Now we have seen that at equilibrium (experimentally realised) $\mu_s = \mu_f$, the chemical potential in each phase being the same, so that—

$$\mu_f^\circ + \boldsymbol{RT} \ln [D]_f = \mu_s^\circ + \boldsymbol{RT} \ln [D]_s \qquad \text{(iii)}$$

The affinity is always reckoned with first attention given to the fibre side, so that the difference $\mu_s^\circ - \mu_f^\circ$ is written $-(\mu_f^\circ - \mu_s^\circ)$ or, using Δ (a common mathematical sign for a difference), as $-\Delta\mu^\circ$. Thus it will be seen, on collecting the terms to the appropriate sides, that equation (iii) becomes—

$$-\Delta\mu^\circ = \boldsymbol{RT} \ln [D]_f - \boldsymbol{RT} \ln [D]_s \qquad \text{(iv)}$$

or—

$$-\Delta\mu^\circ = \boldsymbol{RT} \ln \frac{[D]_f}{[D]_s} \qquad \text{(v)}$$

* The logarithm of 1 is, of course, 0.

When we have decided how to interpret $[D]_f$ and $[D]_s$ in terms of the experimental results, we can thus calculate $-\Delta\mu^\circ$, the affinity.

The form our reasoning has taken has now led to an equation which is not, on the face of it, very complicated, and which bears the characteristic of most thermodynamic statements in that it defines quantitatively and simply certain important common aspects of the behaviour of a variety of systems. It does this by first concentrating on the similarities of the systems and neglecting, for the time being, differences in detail between one system and another. Thus, there is no initial reason why the equation cannot be made to apply to the adsorption of direct, leuco vat, solubilised vat, and reduced sulphur dyes and of substantive coupling components on natural and regenerated cellulose; of acid, direct, basic, and other soluble substantive dyes, and for that matter of chromate ions, on natural proteins and synthetic polyamide fibres; of soluble acetate-rayon dyes on cellulose acetate and other synthetic fibres; etc. But while we may be justified in neglecting the secondary differences between dyes and between fibres in the first part of the treatment, we cannot ignore them when we come to apply our reasoning to specific examples.

Now it is at this stage that snags arise. $[D]_s$ and $[D]_f$ represent figures which show how much the dye is crowded into the bath and the fibre respectively, and which, by implication, show how readily it will go into a bigger space if allowed. The evaluation of these figures, when accurate results are needed, has always presented difficulties to the physical chemist even when dealing with solutions, for there are all kinds of complicating factors. The molecules of a dissolved substance are not, in fact, completely independent. They pull each other and they pull the solvent molecules, and thus to some extent assist or acquiesce in their own crowding together. Crowding would be accurately represented by the actual concentration only if all the molecules in a solution had no size and no attraction for each other, an impossibly ideal situation. Nevertheless, it has been shown that, if we are content with moderate accuracy, and if we do not have our dyebath too strong, we can represent the crowding of the bath reasonably well by the concentration, so that $[D]_s$ might in the simplest case represent the number of gram-molecules of the dye in one litre of bath.

This simple idea would serve if we were dealing with the dye dissolved in the dyebath as whole, undissociated molecules, all in continuous movement, and all seeking unoccupied space into which to migrate. But most of the soluble dyes available to the dyer are salts which, like all other salts, break up as soon as they get into solution, each molecule generally furnishing one "dye" ion, representing the complex, organic, coloured part, and one or more small "colourless" ions of opposite electrical charge. In solution, there must always be close to the dye ion the correct number of the accompanying *counter ions* or *gegenions*. For instance, we can write the molecule of a direct

cotton dye as Na_zD, where z always has a value of at least 2, and may be 4 or even 6. In a molecule of Chlorazol Sky Blue FF, $z = 4$, so that a molecule of this dye in solution will break up into one dye ion and four sodium ions. Thus each complete dye molecule gives rise, when it is dissolved, to five bustling bodies, each striving for more room and to that extent increasing greatly the effective degree of crowding within the dyebath. It has been found in most liquid and gaseous systems that it is the number of actively mobile units rather than the mass of each which really decides the crowding effect. Therefore, to get a truer picture, we must allow for the crowding on the basis of all the mobile units present and not merely on that of molecular concentration. This factor can be shown to make an enormous difference for some dyes. Sky Blue FF, which has already been cited, is a very striking example. Suppose that we had a very strong dyebath containing twice the molecular weight in grams in each litre of the bath. If there were no ionic dissociation, $[D]_s$ would of course equal 2, or more accurately $[Na_4D]_s = 2$. But each gram-molecule will furnish four gram-ions of sodium, so that $[Na^+]_s$ in this dyebath would be $4 \times 2 = 8$, together with one gram-ion of the dye ion, making $[D^{4-}]_s$ equal to 2. Now the contribution of a given unit to the crowding effect increases geometrically, not arithmetically, with the proportion of these units which are formed from the molecule. Thus the contribution of the sodium ions in this case would be $8 \times 8 \times 8 \times 8$ and of dye ions 2, making a total crowding effect of $8 \times 8 \times 8 \times 8 \times 2 = 8192$, i.e. over 4000 times that of undissociated molecules. We may be able to show later that this enormous increase in the total crowding effect for some dyes, due to ionic dissociation in the bath, explains why direct dyes forming ions with high charges, 4 or 6, are extremely salt-sensitive when they are used in concentrated brands.

When we come to measure the crowding of dye in the fibre, we are on much less certain ground. For one thing, not all the space within the fibre is available for dye molecules or ions, and much is taken up by the molecules of the fibre substance. We do not know with complete finality how the dye molecules pack themselves into the fibre. Nevertheless, two particular approaches have been tried, and each, when suitably chosen, has given a reasonable result.

In the one approach, it is assumed that "dyed" dye molecules, attracted by the fibre substance, occupy part of the minute pores and fissures within the fibre, and that the part of the volume they can occupy is about the same as the volume taken up by water molecules when the particular kind of fibre is kept in an atmosphere fully saturated with water vapour. This proportion of water has been determined experimentally, and if its volume is accepted as the volume into which dye is crowded, fairly reasonable results are obtained for e.g. the various forms of fibrous cellulose. This will be discussed in greater detail later.

The other approach is to consider that the dye molecules are absorbed in a single layer on the walls of the pores, forming a kind of mosaic. It is assumed that all the wall surface is covered when the fibre will take no more dye (when it is saturated). If $[D]_{sat}$ represents the condition when every available absorbing area is covered with a dye molecule and $[D]_f$ represents, as before, the actual equilibrium value, then it follows that $[D]_{sat} - [D]_f$ will represent the area of the pore walls which is uncovered, or unoccupied, at equilibrium. The crowding can therefore be represented quite sensibly by the fraction—

$$\frac{\text{Area occupied by dye}}{\text{Area not occupied by dye}} = \frac{[D]_f}{[D]_{sat} - [D]_f} \qquad \text{(vi)}$$

It will be seen that these two approaches are in principle the same, but that, while one expresses crowding within a space, the other expresses crowding upon an area.

Which of these suggested arrangements will best explain the observed behaviour of a particular application class of dye, or even of an individual member of that class, during the dyeing of a particular fibre material, may be difficult to decide upon. On present evidence, however, it is likely that the first mechanism represents the truth more nearly for the dyeing of cellulose with substantive dyes, and that the second corresponds more accurately to the dyeing of natural protein fibres and of synthetic polyamides (nylons) with simple levelling acid dyes from baths of moderate acidity. It may be rather easier to deal with the second example first.

ACID DYES ON BASIC FIBRES

If we consider the dyeing of wool with, say, Naphthalene Orange 2G or Azo Geranine, we find in modern experimental work and calculations a confirmation of views which have long been held about the manner in which the dye molecule is attached to the fibre substance to give the principal stage of dye fixation. It is accepted that the anion of the acid dye— which may be expressed generally as D^-, the dye NaD existing in solution in its ionised form— reacts with basic groups present in the wool structure to form a salt. At the stipulated relatively low acidity, there is normally only one kind of basic group which we need to consider, namely the $-NH_2$ group. In the dilute acid dyebath, this group may be regarded as studding the protein molecules with a series of non-mobile ionised ammonium groups $-NH_3^+$. The fixation of the coloured dye ion by the wool is thus conceived as the reaction—

$$-NH_3^+ + D^- \rightarrow -NH_3D$$

The detailed knowledge that exists about the structure of the wool fibres suggests that, in the parts of the fibre which are chiefly responsible for the absorption of dye, these basic groups are relatively small in number, as compared with the other parts of the fibre molecules, and are well separated from one another. We can therefore picture the walls of the microscopic fissures in the fibre, by which the dye ions must enter and penetrate, as being studded at intervals with these

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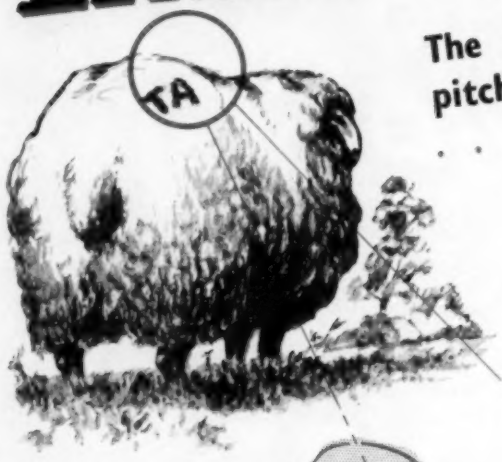

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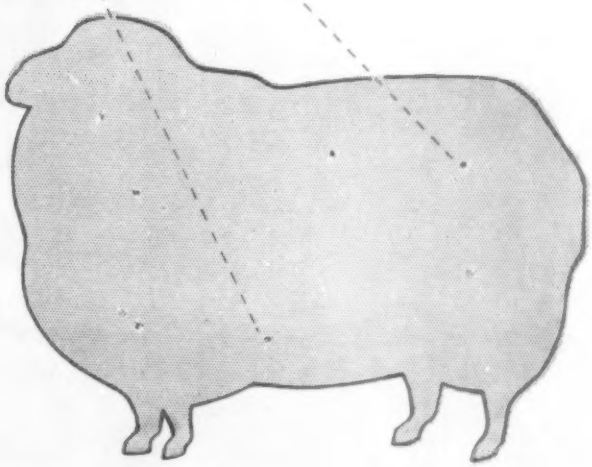

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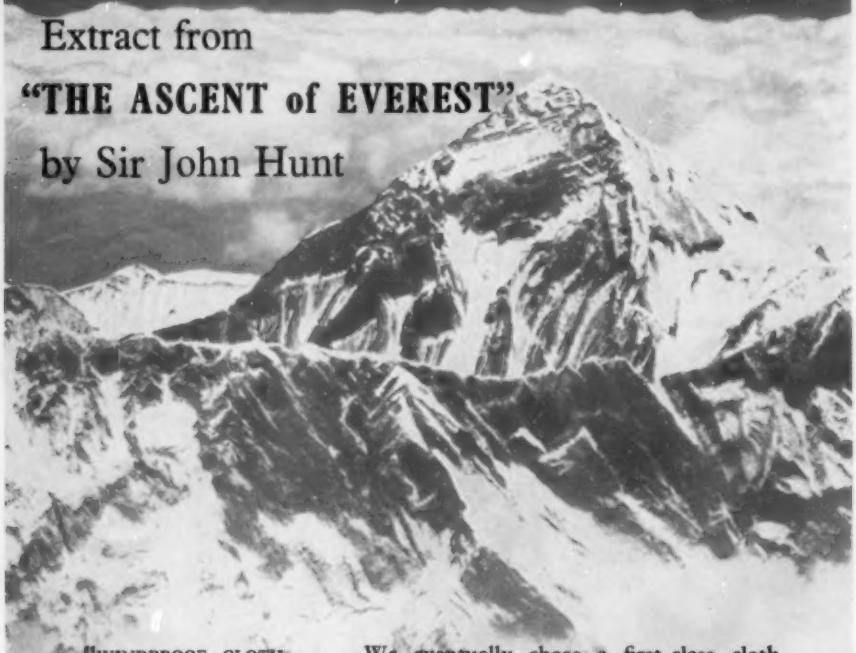

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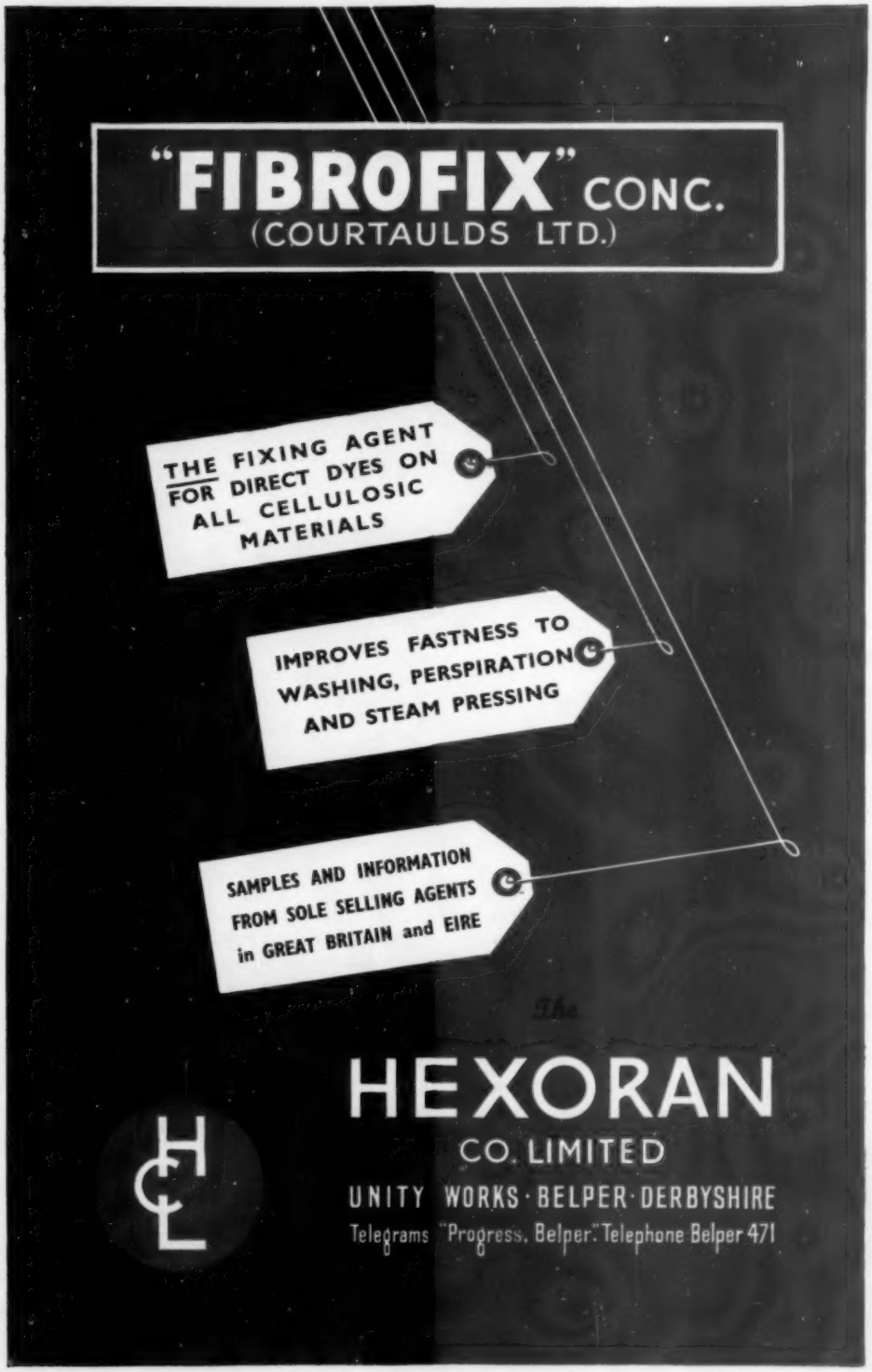
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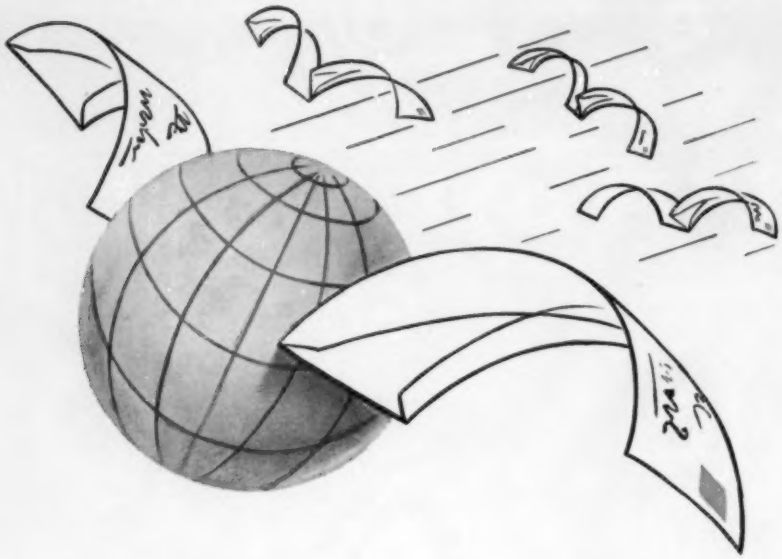

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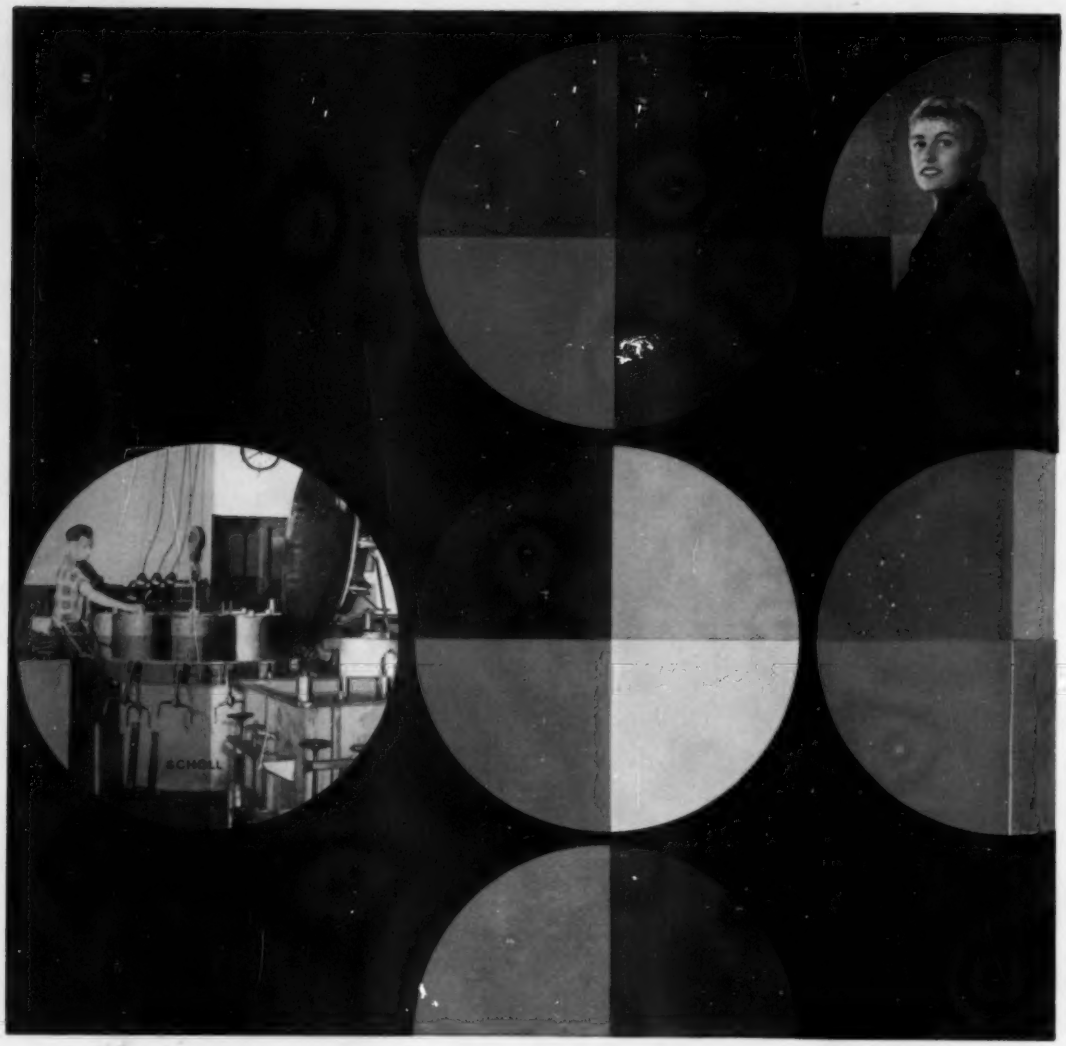

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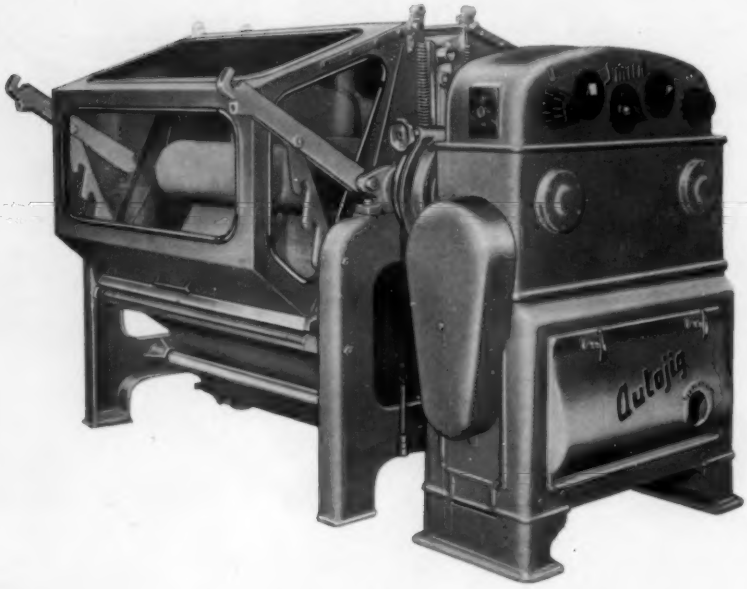

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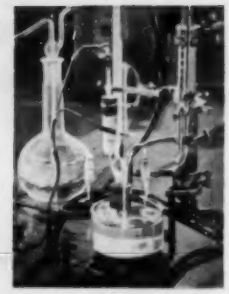

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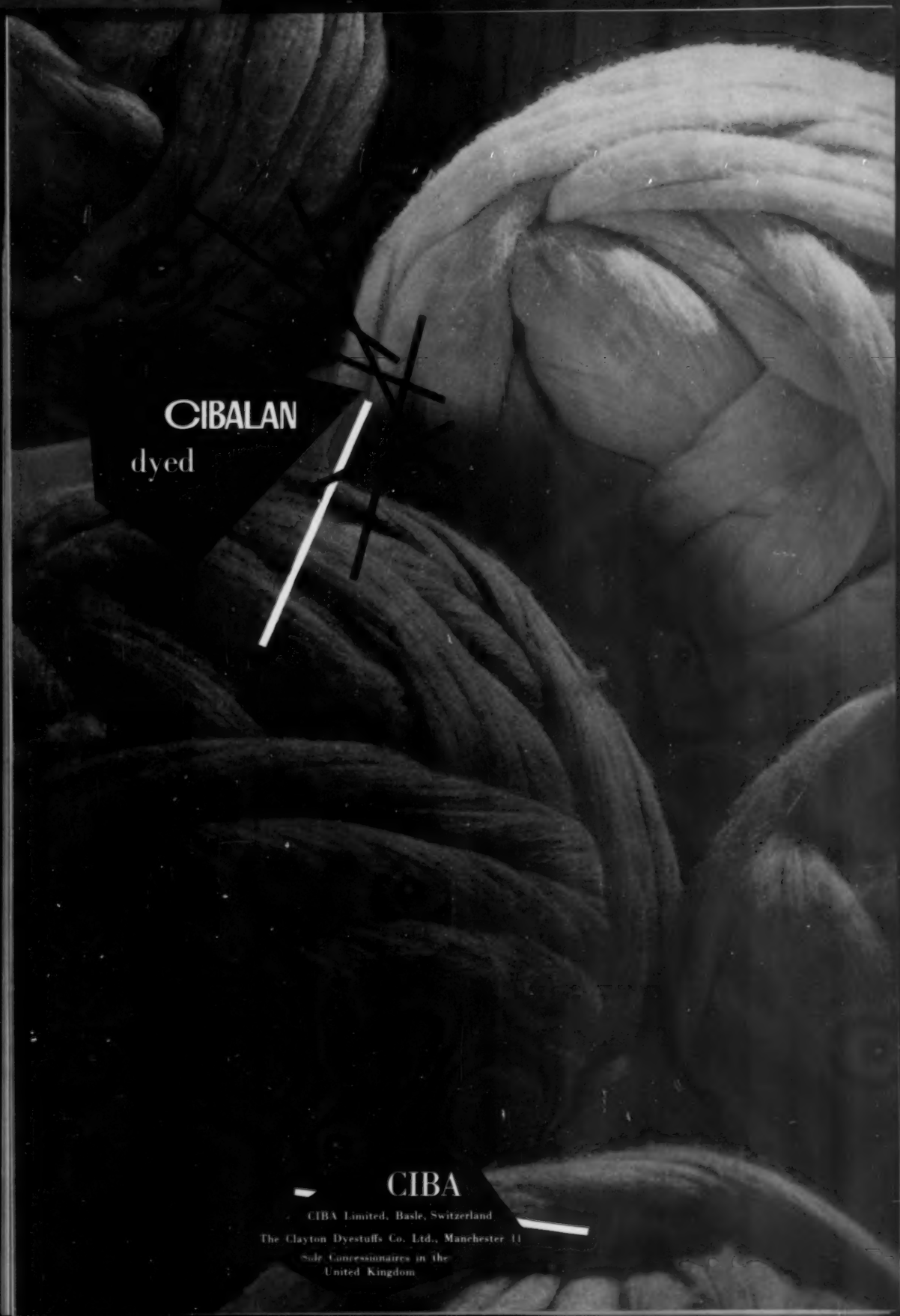
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He wears an ermine-lined boemio, or half-length dress cloak, without a cowl. He wears also the Spanish type of doublet, or jubón, decorated with bands of braid and opening down the front with a large number of buttons. The trunks are voluminous, but their linings have not been pulled out between the panes in the German-Swiss fashion. The beginnings of the ruff are discernible in the neckband, which like the wristbands is now pleated and fluted.

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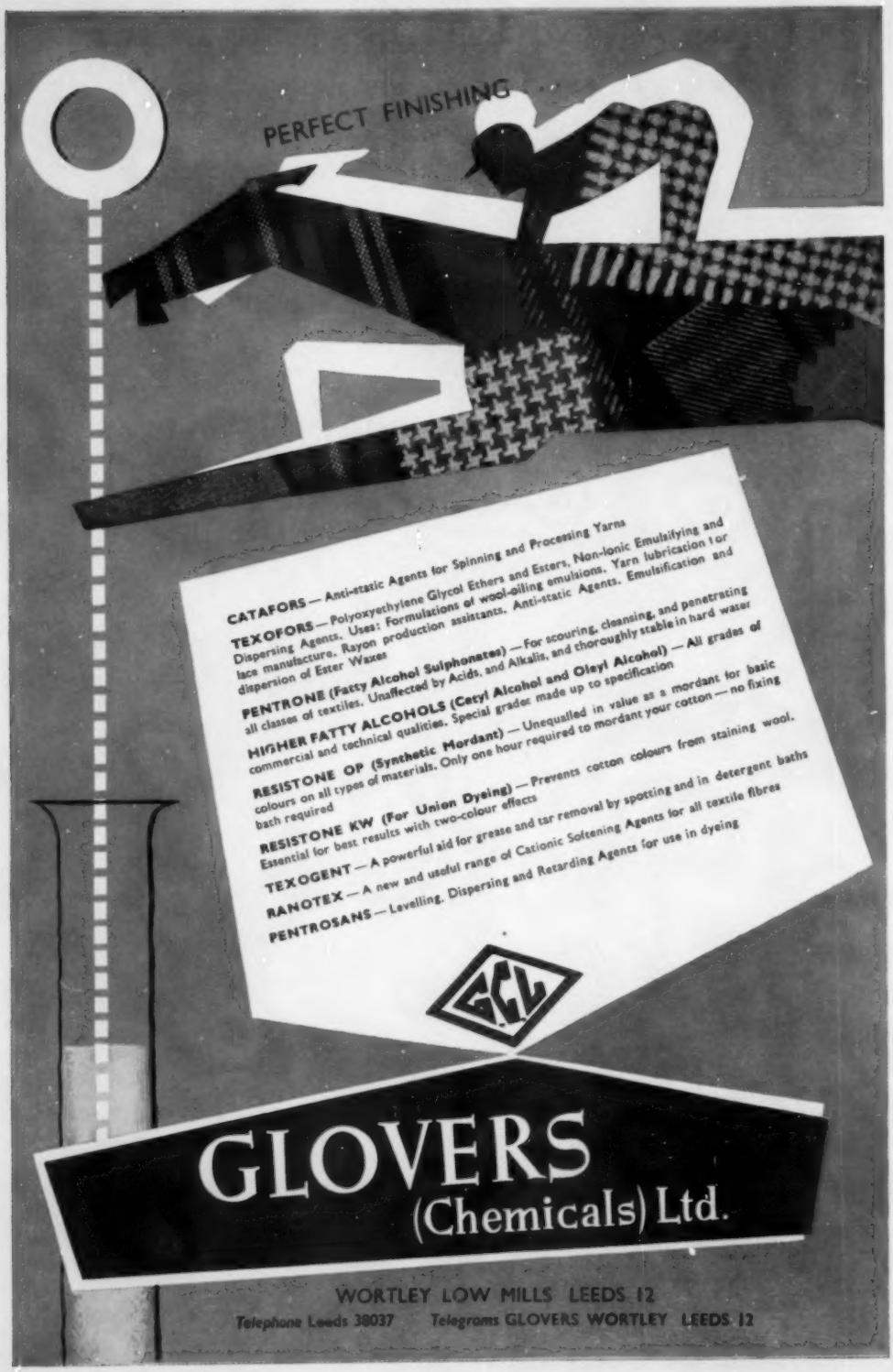
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basic groups. As dye ions enter the fibre they combine one by one with these basic groups, and so are anchored to the wall by the same kind of electrical force—the kind which operates between a positively and a negatively charged body—as that which holds the sodium and chlorine together in solid sodium chloride. Electrical forces which act when oppositely charged ions come into each other's vicinity have a long range of action. Although they weaken as the individual members of the pair of ions are separated, in the same way that the force between two magnets diminishes on separation, they are still effective for relatively large distances, many times the dimensions of a carbon atom. This means that a very close approach of the dye ion to the basic ionic group on the walls of the fissure is not necessary for effective anchoring to take place. Just as a fixed weight of ammonia, representing a fixed number of ammonium ions, will combine only with the equivalent number of chloride ions, so, within fairly close limits, there is a corresponding equivalence between the basic groups in the fibre and the dye ions which combine with them. Thus, when sufficient dye ions have entered the fibre substance to combine with all the basic groups which are accessible there, fixation, or at least definite and strong fixation, of the dye ion will cease. This condition is said to correspond to saturation of the fibre with the dye. It will be seen that, providing allowance is made for the number of ionic charges on the dye ions, we should always arrive at the same value for the number of basic groups in a given fibre by saturation experiments, no matter what dye we use, and, if our reasoning is correct, we do not need to use dye ions for our determination, but can use simple ions like chloride, sulphate, or those of other strong acids. This proves to be true, and there is a very satisfactory agreement in the results of most of these methods for the proportion of accessible basic groups in wool. It amounts to between 0·8 and 0·9 gram-equivalent weights of basic group for each kilogram of the dry fibre. The picture which is deduced from this, of dye ions attached one by one to the basic groups in the fibre (with no piling of these ions on top of each other) until the whole of the internal absorbing surface is occupied with dye ions at its active points, leads naturally to the description of crowding of the dye in terms of the closeness, in any given dyed fibre, to full saturation. Hence we derive our expression—

$$\text{Degree of crowding} = \frac{\text{Active sites occupied}}{\text{Active sites vacant}} = \frac{\text{Equivs. of dye taken up}}{\text{Equivs. of dye at saturation} - \text{Equivs. of dye taken up}} \qquad \text{(vii)}$$

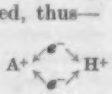
The same kind of reasoning will apply for the absorption of acid dyes on other protein fibres and on nylon, and, with the necessary inversion of emphasis, for the absorption of basic dyes through the acid groups of protein fibres. Apart from the remarkable agreement in the experimental evidence provided when a saturation value for, say, wool is determined with different kinds of anion, there is other confirmatory evidence for the ideas just outlined. It is possible to change some of the amino groups in natural proteins into hydroxyl by suitable treatments with nitrous acid. When this is done, there is a corresponding drop in the saturation value for dyes and for other anions. Similarly, when the amino groups in nylon, which are responsible for the absorption of acid dyes applied from baths of moderate concentration, and which are comparatively easy to ionise, are changed by acetylation into acetamido groups, which are difficult to ionise, the absorption on the nylon shows a corresponding fall.

DIRECT COTTON DYES ON CELLULOSE

When we come to consider the dyeing of cellulosic fibres—cotton, linen, and viscose and cuprammonium rayons—with substantive dyes, we find that the picture that has emerged for the dyeing of wool will not fit the experimental facts until it is modified. Before we look for any more profound causes for these deviations, there is one fact which must be kept in mind, for it may set a limit to the amount of simplification which can be justified. The smallest typical direct dye molecule, in which the characteristic non-ionic substantivity for cellulose is shown, like Congo Red, for instance, has more complex and more specific structural features than the simplest representatives of the acid dyes which we have just been discussing. With this qualification, however, modern work has shown that the main distinction from the purely acid dyes (for the direct dyes themselves are acid dyes on a strictly chemical classification, and will in fact dye protein fibres under suitable conditions) lies in the manner of linkage of the dye to the fibre-substance. The current theory assumes that this linking is by "hydrogen bonds" between hydroxyl groups on the cellulose and certain groups, including $-NH_2$, $-OH$, and $-N{:}N-$, in the dye molecule. As the concept of hydrogen bonds is rather less familiar to many than the more "classical" types of chemical bond, perhaps a word or two in amplification may be welcome.

HYDROGEN BONDS

We have already been dealing with one kind of valency, called *electrovalency* by the chemist, in which powerful and long-range attractive forces are set up between oppositely charged *ions*, i.e. atoms or groups of atoms that have either lost (*cations*, positively charged) or gained (*anions*, negatively charged) electrons beyond the normal atomic complement of these bodies. Another well established, powerful kind of bond is the *covalent link*, which, for instance, holds many of the carbon atoms together in organic compounds. This bond is formed when one electron is eased a little away from each of the atoms which are to combine, leaving the rest of the atom positively charged. Then each residue exercises some electrostatic pull on each of the electrons that have been partly detached, thus—



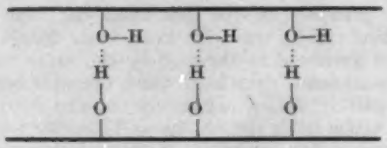
so that in this way the two atoms, which we may call A*e* and B*e*, are linked by the electrons which they share between them. This is the kind of link which the classical chemist would write C–C in, say, H_3C–COOH, and which the modern chemist, if he found it necessary to particularise, would write C:C. On this system, hydrogen would be attached to carbon in, say, methane by shared electrons C:H or to oxygen in ethyl alcohol or phenol thus O:H. But, in the latter combination, the oxygen does not play quite fair. Owing to its particular atomic build, detachment of electrons from the oxygen atom is rather harder than from the hydrogen atom. Thus, when sharing is going on, we find the electrons rather further over in the territory of the oxygen than they are in the territory of the hydrogen, something like this—

Thus on near approach to the OH group the oxygen residue is, on balance, a little more negative than it would be with impartial sharing of electrons, and the hydrogen a little more positive. Thus if two molecules can approach each other so that their hydroxyl groups are in very close proximity, an attraction can be set up between the slightly positive hydrogen of one and the slightly negative oxygen of the other, and a new bond, what might be called an "extra-atomic bond", can be formed between the two molecules—

$$M^1\text{–}O^-\text{–}H^+ \;+\; \overset{H^+}{\underset{|}{O^-}}\text{–}M^2 \;\rightarrow\; M^1\text{–}O^-\text{–}H^+\cdots\overset{H^+}{\underset{|}{O^-}}\text{–}M^2$$

This is the hydrogen bond.

In modern atomic physics there are other ways of explaining the formation of hydrogen bonds, but this one should serve, at any rate, to remove some of the mystery for those who were brought up on classical theories of valency. Two important observations have to be made. The first is that the hydrogen bond is weak compared with electrovalent (ionic) and covalent bonds. The other is that its strength diminishes with great rapidity as the groups between which it is operating are moved apart. From these properties, two important consequences follow. When two molecules are linked by a single hydrogen bond, operating, shall we say, between a hydroxyl group in each of them, the union is quite weak, and it does not take much to separate them. The battering they can get from solvent molecules, or their own movements, as the temperature is raised, soon overcome the linking. If, however, the molecules are extended in one or two dimensions, each having a number of groups capable of forming hydrogen bonds, and being so shaped that they can lie side by side and a number of bonds can form between them, then the attachment of the two may be very strong, and they may strongly resist separation. This is what is supposed to happen when the chain molecules of cellulose are arranged closely together—



The united effect of many of these weak bonds contributes to a structure which is very difficult to get apart. As is generally known, there are only a few, rather exotic solvents, like cuprammonium hydroxide solution and concentrated sulphuric acid, which can do this, and they are effective only because they have special powers of interfering with the hydrogen bonds in the cellulose.

The second important consequence follows from the short operating range of hydrogen bonds. For molecules which they are to bind tightly together, not only must there be present in each molecule a number of groups capable of forming hydrogen bonds, but the shape of the molecule itself and the disposition of these groups must be such that, when the two molecules approach closely together, each group on the one must find, extremely close to it, a corresponding group on the other molecule. There has therefore to be an accurate overall fitting of the molecules, and a close similarity in the spacing of the groups in each. When the two molecules are of the same kind, this may not be particularly difficult, and this is one of the ways in which we can encourage aggregation of dissolved dye molecules. Where the molecules to be joined are different, a dye molecule and a fibre molecule for instance, then this coincidence is either accidental, as it was when the first direct dye was made, or deliberate, as it must be now when new direct dyes are projected.

SHAPE OF MOLECULES OF DIRECT COTTON DYES

The characteristic features in the structure of the molecule of any compound which shows the behaviour peculiar to the class of direct cotton dyes are four—

(i) The general shape is long, narrow, thin, and flat.

(ii) There must be a number of groups, e.g. –OH, $–NH_2$, –N:N–, all of which can form hydrogen bonds with the –OH groups of cellulose. For most of the direct dyes, this follows as a consequence of the synthetic methods used for making the correct kind of long molecule, and also, to an important degree, for producing a molecular structure which will lead to a coloured substance.

(iii) These hydrogen-bond-forming groups must be spaced along the length of the molecule so that certain pairs of them are exactly, or very nearly, the same distance apart as some of the hydroxyl groups which are regularly spaced along the length of the cellulose molecule. One such spacing is about 10·3 Ångstrom units (ten-millionths of a millimetre) in cellulose, and the spacing in a direct dye molecule might be about 10·8 A.

(iv) The presence of two or more ion-forming groups, usually $–SO_3Na$, to help the dye to dissolve

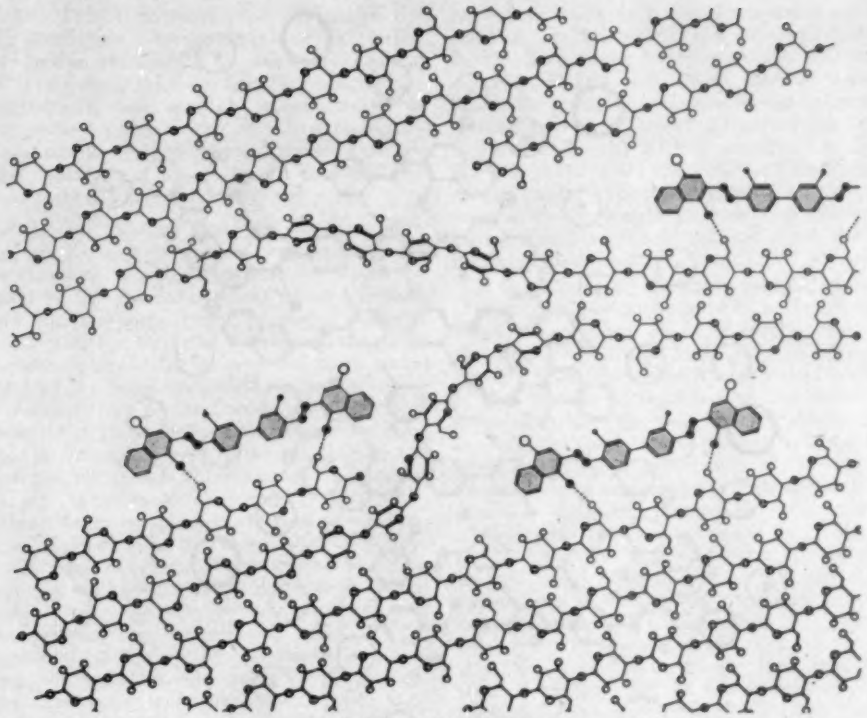
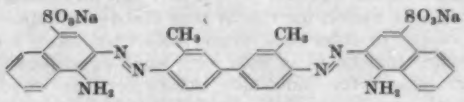


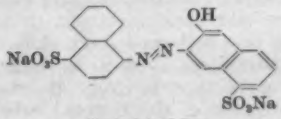
FIG. 1—Attachment of Direct Dye Molecules to Cellulose Chains in Fissures of Fibres[1]

in water, and at some part of the molecule remote from the hydrogen-bond-forming groups, so that the operation of the latter is not interfered with.

With all these requirements fulfilled, it will be seen from Fig. 1 how a typical direct dye molecule can align itself alongside a cellulose molecule forming part of the wall in one of the minute fissures in a fibre, and be attached to it by two hydrogen bonds simultaneously. These are sufficient to produce a fairly strong attachment, a useful affinity. It will be seen also, from the chemical formulae—



Typical Direct Cotton Dye
(Benzopurpurin 4B)

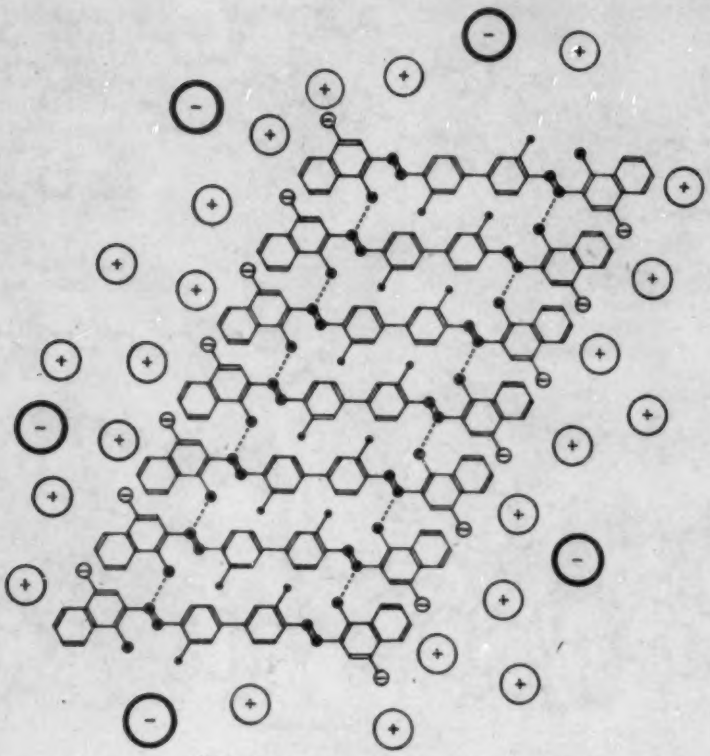


Typical Acid Dye
(Naphthalene Red EA)

that a representative acid dye, although its molecule possesses essentially similar substituent groups to the direct dye, can never hope to form more than one hydrogen bond with cellulose, and this coincides with the very low affinity of these dyes for purely cellulosic fibres. We will see a little later whether we can give numerical values to this strength of attachment.

CONCENTRATION OF DYE IN THE FIBRE

It might be thought that the short range of action over which hydrogen bonds are effective, and the necessity for registration between dye molecules and cellulose molecules, would lead to a state of affairs in which the absorbing cellulosic walls of the internal fissures in the fibre would become progressively coated with a single layer of dye molecules until ultimately all the convenient pairs of hydroxyl groups in the cellulose would be engaged in holding molecules of the dye. Then saturation should be achieved. It is, however, extremely difficult to get consistent values for the direct dye content of cellulose at saturation, in contrast to the dyeing of wool with acid dyes. Various reasons have been suggested for this, some of which, in the absence of a more detailed picture of the internal structure of the fibre, would be difficult to explain. One reason is, however, fairly easy to picture. From Fig. 2 it will be seen that the very conditions which permit the formation of two hydrogen bonds between a dye molecule and cellulose can favour the attachment of one dye to another. This can make the dye readily



⊕ Sodium cations.
⊖ Chloride anions (if common salt is present)

FIG. 2 — Several Dye Molecules in a Crystal [1]

aggregate in solution, and it can mean that, when one dye molecule has been dyed on the cellulose, other dye molecules can be dyed on the one first attached. Thus it does not follow that one small area of space on the pore wall can be regarded as fully occupied when one dye molecule is affixed there. A further, indefinite number may pile up on the same space. If things like this are happening, it is manifestly incorrect to calculate the crowding of the dye molecules within the fibre on the basis of the internal wall space they may occupy. It seems much more reasonable to suggest that the crowding should be calculated in terms of the completeness with which the dye in the fibre occupies the pores and fissures which are qualified by their size or shape to permit the entrance of dye molecules.

VOLUME OF DYEING SPACE IN THE FIBRE

It is, of course, impossible to measure directly the proportion that these pores and fissures occupy in the total volume of a given weight of cotton or of some other cellulosic fibre, so that any volume that is accepted must first be deduced from circumstantial evidence. There has been much work carried out in attempts to obtain some information on this question. Refined measurements of the density of the fibre have been made in an effort to see how much of the fibre is solid cellulose and how much is empty space. The absorption of various substances with molecules of known dimensions has been studied to find how big a molecule must be before it becomes too large to enter the pores.

Now it must be remembered that practically all the dyeing with which we are concerned takes place from aqueous dyebaths. An immediately obvious reason for this is that the dye requires a solvent in order that it may be broken down into single molecules, or into very small aggregates of at most a few molecules; otherwise there can be little possibility of the dye being able to penetrate the fibre structure. The water has, however, another function. It can first enter into the pores of the fibre and open them out from what we conceive to be a collapsed form when the fibre is dry. Cellulosic fibres do swell markedly in water, the swelling being principally the accumulated effect of inflation of the internal submicroscopic capillaries. This swelling is, in fact, an essential prerequisite for dyeing. There is no dyeing of cellulose when alcohol is used instead of water, even though the dye itself may be soluble in the solvent, for the swelling of the fibre is then

negligible. Thus it is incomplete to talk of the "dyeing of cellulose": we should talk of the "dyeing of *water-swollen* cellulose". In this condition, the entries to the capillaries are large enough for the dye particles to enter, and the pores themselves contain water, which keeps the dye molecules apart and mobile so that they can diffuse through the fibre until they are at length attached by chemical forces to the pore walls.

It might be thought that the effective pore volume, upon which the internal concentration of dye in the fibre should be calculated, would be measured by the volume of water which has been imbibed into the pores during prolonged soaking. This value would be too great, for some of the water in the wider pores must be regarded more as an extension of the outer dyebath into the fibre than as an essential part of the fibres themselves, just as the water in the middle of an estuary must be regarded as belonging more to the sea than to the land. What we need is the maximum volume of the "lining" of dye molecules round the pore walls, the volume taken up by dye which is attached to cellulose molecules or to other dye molecules within the range of action of hydrogen bonds. Here reasoning by analogy has had to be adopted. When dry cellulose takes up water from the water vapour in the surrounding atmosphere, most of the absorption is effected by hydrogen bonding between the cellulose and water molecules, or between one water molecule and another. It is assumed that they will line the absorbing surfaces inside the cellulose to a depth which is not very different from the depth of the lining of dye molecules. This, at first sight, may seem rather a surprising assumption, because the dye molecules are so much larger than the water molecules, but it must be remembered that we have evidence that the dye molecules align themselves parallel to the cellulose chains in the walls. As the dye molecules are long and thin and flat, it will be seen that the cross-sectional dimensions, which are the important ones in deciding the thickness of the lining, are not greatly different from the dimensions of water molecules, and the ranges of the attracting forces will also be of the same order in each case. It has been found that cotton will take up a total of 0·22 litre of liquid water for each kilogram of the dry fibre-substance when it is maintained for a long period in an atmosphere saturated with water vapour at 90°C. This is therefore taken as the proportional "lining" volume which can be occupied by adsorbed dye.

To take a specific example, suppose that in a given dyeing 1 kg. of dry cotton takes up 10 g. of a dye whose molecular weight is 500. Then, for the purposes of an affinity calculation, the effective molar concentration (M. gram-molecules per litre) of the dye in the fibre will be—

$$\frac{10}{0{\cdot}22 \times 500} = 0{\cdot}091 \text{ M.}$$

Suppose, further, that we have been dyeing from a bath of the pure dye, so that the presence of salt has not complicated the issue, and that the dye we have been using is unibivalent, being present in solution as $2Na^+$ and the coloured ions D^{2-}. In the fibre itself, therefore, there will be 0·091 gram-ion of D^{2-} per litre of internal space, and $2 \times 0{\cdot}091$ gram-ion of sodium in the same volume. Referring to p. 36, we thus see that the crowding factor for dye in the cotton fibre is $[Na^+]^2 \times [D^{2-}]$ or $0{\cdot}182 \times 0{\cdot}182 \times 0{\cdot}091$. This assumption of the water-vapour-absorption volume as the volume of the maximum receptive space in the fibre is found to give results that are of the correct order of magnitude.

It is understood, of course, that different values of this "lining" volume have to be found for other forms of cellulose, e.g. 0·46 litre/kg. for normal viscose rayon and 0·37 litre/kg. for cuprammonium rayon. Apart from this, the chemical mechanism of dye uptake is regarded as the same for all forms of cellulose, so that the only change made in the affinity calculation in passing from one form of fibrous cellulose to another is the change in the value given to this receptive volume, or V as it is generally denoted. It may be thought that the analogies between the uptake of dye molecules by the fibre and the uptake of water molecules would be sufficiently close to give results in the affinity calculations of the correct order but not strictly accurate values. This is indeed true: work done comparatively recently shows that the value of V should be appreciably greater than that deduced from the absorption of water vapour. Various corrections for secondary effects have had to be made, a full treatment of which at this place would disturb the clarity of the picture. Nevertheless, the method appears to be basically sound, and two workers in particular— Marshall and Peters [2]— have used it for a long examination of a series of dyeings of twelve direct dyes on different forms of fibrous cellulose over a range of temperatures from 50° to 100°C. The results of this work form a good general example of the way in which affinity is calculated, and the significance of the values which are obtained. First of all, with all the dyes examined, it is found that the affinity gets less as the temperature rises. This is a reflection of practical experience when dyeing is carried to equilibrium.

AFFINITY VALUES FOR CELLULOSIC FIBRES

For dyes which were examined in detail, Marshall and Peters [2] found that the calculated affinity was not very different for any one dye applied to different forms of cellulose. Thus, for Chrysophenine G at 90°C. the values of $-\Delta\mu^\circ$ in the appropriate energy units are— cuprammonium rayon 2800, viscose rayon 3100, bleached cotton 3000, and mercerised cotton 3100. Very similar sequences are obtained with other dyes, and this is a striking confirmation of the original postulate, viz. that when it is regarded as a combination between the chemical entity cellulose and the dye molecule, the direct dyeing process is largely independent of the accidents of molecular arrangement within the fibre.

The argument can be carried further. Still selecting the results at 90°C., although those at the

other temperatures would do almost as well, it is found that the affinity values for all twelve dyes on all the fibre substances lie between 3000 and 6000 units. Considering the wide range of practical dyeing properties represented by the selection of dyes used (anything between Chrysophenine G and Chlorazol Brown M) and the assumptions that have to be made in developing the theory, this is a very strong indication of the essential similarity of the chemistry of direct dyeing processes no matter what dye is used. The results may be calculated in a slightly different way. Taking the value for the affinity of a dye, and the extent to which it changes with rise in temperature, a new value, the *heat of dyeing*, can be calculated. This is a measure of the amount of heat energy which is furnished when a standard weight of dye combines with cellulose in the dyeing process. It is small and not easy to measure directly. The values so calculated range from about 15,000 to 20,000 units among the different dyes. There is independent evidence that, when all the molecules in one gram-molecular weight of a substance become attached to other molecules by one hydrogen bond each, the amount of energy given out is somewhere around 5000 units. From this it has been deduced that either attachment of direct dye molecules to cellulose is taking place with the formation of three or four hydrogen bonds, certainly more than two; or, in the absence of more detailed information, two hydrogen bonds are essential, and they are assisted by other subsidiary chemical forces which we know to exist, but which have not been discussed in the present simplified treatment*.

AFFINITY IN PROTEIN FIBRES

We have considered at some length the application of the idea of affinity to obtain a numerical value for the strength of attachment of direct dyes to cellulosic fibres, and we have all the time been looking to see how far our results are consistent with the idea that the dye molecule is attached to the fibre by more than one hydrogen bond. Let us see how far similar treatments can be informative for the dyeing of protein fibres with acid dyes. Here, it has already been stated that the initiation, at least, of the dyeing process comes from the formation of electrovalent chemical bonds between the coloured dye anion and basic groups in the fibre-substance. While the essential thermodynamic reasoning is the same for this kind of dyeing as for the dyeing of cotton, it is very likely that modification of the details will be necessary in comparing the behaviour of fibre-substances so dissimilar both chemically and physically as wool protein and, say, cotton cellulose. A very important factor which must be considered is the true acidity or pH of the dyebath. If the bath is not too acid, the amino groups in the fibre become ionised and form the points of attachment for the dye—

$$-NH_2 + H^+ \longrightarrow -NH_3^+$$

*To give point to our opening verse, and to drive home the lesson that nothing is fixed in scientific thought, it should be mentioned that Dr. R. H. Peters has recently pointed out grave objections to the hydrogen bond theory.

When the solution is very acid, a new set of groups, the secondary amino groups, come into operation—

$$>NH + H^+ \longrightarrow >NH_2^+$$

However, this represents rather extreme conditions, and the combination with amino groups can be studied alone. There are some interesting peculiarities of this kind of dyeing. Firstly, we have seen that combination of the fibre-substance with the coloured acid representing an acid dye is fundamentally no different from the combination with simpler, colourless acids, such as hydrochloric, or organic acids like the naphthalenesulphonic acids. All these should have an affinity for protein fibres, and so they have. Determinations yield values ranging from 5300 units for hydrochloric acid at 0°C. to 10,000 and more for some aromatic sulphonic acids at the same temperature. As might be expected, the affinities of acid dyes themselves vary according to the structure of the dye and the conditions under which it is applied, but values varying from about 4000 to 24,000 units have been obtained. The affinities of the acid dyes for their appropriate fibres seem to cover the numerical range of those of the direct dyes for cellulose, and even, in some cases, to exceed it, which is a reasonable reflection of technical behaviour. The significance of affinity values of acid dyes on wool is shown in one of the methods used to obtain data from which the values could be calculated.

A great deal of work has been done on the determination of the affinity of acid dyes on wool, and some points about the exact interpretation of experimental values have led to a controversy which is not yet resolved. The problem has wider implications than the corresponding uptake of direct dyes by cellulose, for, as we have seen, it concerns a very well known and widely occurring type of reaction, the neutralisation of a base with an acid, occurring in highly specialised circumstances. Moreover, this fundamental reaction need not necessarily be studied entirely as a dyeing process, for it can start with the absorption of very simple acids like hydrochloric and sulphuric, and then through a series of organic acids of increasingly complex molecular structure, until finally the acid dyes themselves are used. The whole field of the study of dye affinity by thermodynamic methods widened very rapidly after work by Gilbert and Rideal in Cambridge had been published on the combination of various acids with wool, the results of their experiments being given a general form in the now famous Gilbert–Rideal equation. This equation has the same form and the same functions as the affinity equations which we have already discussed in some detail. This widening of the field of application of the thermodynamic treatment has some interesting consequences. A well known effect in the dyeing of acid dyes is the restraining action of neutral salts such as sodium sulphate and chloride upon the absorption of the dye. This is explained by assuming that the chloride or sulphate ions provided by the added electrolyte can compete

with the dye anions for combination with the basic groups in the fibre. Therefore, from a dyebath containing both electrolyte and acid dye, the relative proportions absorbed of the chloride or sulphate ions on the one hand, and the dye ions on the other, will depend upon two factors— (i) the relative proportions of the two ionic species in the bath, since it is common sense that the more numerous the particular ion, inorganic or dye, the greater its chance of getting to and occupying the basic sites, and (ii) the relative affinities, as already defined, of the two species. If the affinity of the dye ion is high, i.e. if it can hold on relatively tightly to the fibre molecule once combination has occurred, we shall expect to find that the proportion of it present in the fibre at the end of dyeing has increased and that the proportion in the bath has diminished. By comparing ions at a standard concentration, it can easily be shown that one ion can displace another from combination with the fibre in proportion as its affinity is the greater. This was proved by Gilbert and by other workers, notably Vickerstaff and his collaborators, in the following manner. The affinities of a number of acid dyes on wool were determined by methods which were only a refinement of the ordinary methods of direct dyeing. Then fresh dyeings of each dye were made, and allowed to stand until equilibrium had been reached in a blank dyebath of dilute sodium chloride, so that the chloride could displace some of the combined dye. From the relative proportion of the dye desorbed, and an independently determined value for the affinity of the chloride ion, the affinity of each dye was calculated. In a third set of experiments, wool was dyed to equilibrium in a bath containing two acid dyes initially present in known proportions. The affinity of one dye was assumed from other experiments, and from the relative amounts of the two taken up, the affinity of the other dye was calculated. It was found that the affinity of the dye selected came to almost the same value, no matter by which of the three methods it had been determined. The prediction of how much of each component of a dyebath containing a number of dyes will be taken up by a fibre under specified dyeing conditions is an important use for the theory of affinity.

MEGGY'S THEORY

Another view of the mechanism of dyeing, put forward by Meggy as a complement or as an alternative to the acid–base theory of wool dyeing with acid dyes, deserves a little consideration on its own. It is an interesting theory because it sees the molecules of certain acid dyes as similar in chemical make-up and properties to the molecules of soap, or, more particularly to the molecules of synthetic wetting compounds, such as, for instance, Lissapol C (ICI) and Teepol X (Shell). Recent successful work has been inspired by this idea. Many dye molecules have large regions which are wholly aromatic or aliphatic in constitution, i.e. which contain only carbon and hydrogen. These parts attract the molecules of water very feebly, and a substance whose molecule had no other type of structure in it would be as insoluble as a mineral oil or a wax. If other groups, like hydroxyl, carboxyl, and sulphonic acid, which attract water strongly, are attached to the molecule, then the solubility in water can be increased more or less at will according to the water-holding capacity of the new group or the number present in the molecule. We see this device in operation in many fields of dye chemistry where a coloured compound, which may have too great a proportion of hydrocarbon groups in its molecule for it to be readily soluble in water, is changed from a pigment to a soluble dye by sulphonation. Now, if it were possible to introduce a single molecule of a purely hydrocarbon compound, such as naphthalene, into water, we should find that it would have great difficulty in remaining there. By its entry, it would have to push apart several molecules of water against the strong attraction, exercised mainly through hydrogen bonds, which one water molecule has for each of its immediate neighbours. As the hydrocarbon molecule itself has little attraction for water, the separated water molecules have, so to speak, nothing to hold on to. In consequence, they try to re-establish the bonds which formerly existed between them by ejecting the naphthalene— rather in the same way as a piece of waxed paper would be shot to the surface if it were plunged under water and then released. Imagine what would happen to the naphthalene molecule if it could be heavily sulphonated, say, with three or four sulphonic acid groups. Then there certainly would be something for the water to hold on to, and such a molecule would be accepted into the body of the water to stay there permanently as part of a homogeneous solution.

Suppose, however, that the degree of sulphonation were substantially diminished to give, say, only one water-attracting (*hydrophilic*) group for each molecule of the naphthalene derivative. Then a state of balance may be envisaged, in which the tendency of the hydrocarbon part to be ejected from the water would just be opposed by the ability of the sulphonic acid group to keep it in the water. A compromise is reached in which the molecule comes to a free surface of the solution, and remains there partly in and partly out. An analogy might be provided by a fishing float with a sinker attached, in which the buoyancy of the float is only just able to oppose the weight of the sinker. This mechanism is an essential feature of the action of wetting agents, the molecules of which gather at any new surface that may be produced between their solution and a body to be wetted.

Meggy has given experimental results which show that groups in certain acid dyes that should be responsible for the attachment of the molecule to a basic group in wool protein, and should make the dye very soluble in water, are not so active in either of these functions as might be expected. This is due to a form of internal linking, known as *coordination*, with other groups in the dye molecule. The active groups have thus less chemical attraction to spare, either for the water molecules, encouraging solution, or for the basic groups in the fibre-

substance, encouraging absorption and fixation. Nevertheless, these dyes, best represented by fast-to-milling dyes of the Carbolan (ICI) type, can give dyeings which are quite fast to water and to other wet treatments. It is Meggy's contention that the adsorption of dye is due less to chemical attraction between the dye molecules and the fibre substance than to an eviction of the dye molecules from water, whence they go to the only place where they can be received, that is to say the wool. There are certain parts of keratin chain molecules which are predominantly hydrocarbon in constitution, e.g. the middle regions of the side-chains, and it is thought that these can exercise an action akin to solution on the hydrocarbon parts of the dye molecule, very much as white spirit will dissolve paraffin wax. To sum up, we have a theory, supported by both analogy and direct evidence, which seems to be an inversion of the uptake of substantive dyes from dilute aqueous solutions. The dye, instead of being pulled out of solution by an attraction for groups in the wool molecules, is pushed into the wool by the half-hearted solvent, water.

SOLID SOLUTION AND THE DYEING OF CELLULOSE ACETATE

What has just been said leads to the ideas that have been put forward to explain a mechanism for the dyeing of cellulose acetate and other ester and amide fibres. Cellulose acetate differs from the natural fibres and the regenerated cellulose fibres in that its ability to take up water, either from moisture in the atmosphere or from surrounding liquid water, is much less. This is not surprising if we compare its chemical constitution with that of chemically unmodified cellulose. Much of the power of cellulose to take up and retain water may be referred to the ability of the hydroxyl groups to form hydrogen bonds with water molecules. In cellulose acetate, five out of every six of these hydroxyl groups have been replaced by acetoxy radicals, and this diminishes hydrogen bond formation. Since the cellulose acetate cannot take up much water, it cannot swell very much in aqueous dyebaths, and this might be thought to limit the ability of large dye molecules to penetrate the pores and fissures of the fibre and to be adsorbed on internal fibre surfaces. It was observed, right from the time when the first attempts were made to dye this class of fibre, that the more water-soluble a dye, the less it was taken up by cellulose acetate, unless some extraordinary expedient were employed. It seems paradoxical, in the light of experience with the conventional fibres, that the dyes which can be taken up readily are those which are very sparingly soluble or which do not dissolve in water at all, but are employed as suspensions in which the particles, however fine, are still too large to enter the pores of the fibre. These dyes will, however, dissolve in a variety of organic solvents, particularly esters such as butyl and amyl acetates, and in acetone, solvents which will dissolve also cellulose acetate itself. This has led many to put forward the concept of "solid solution", in which a similarity is seen between the dyeing of the fibre from aqueous suspension and the extraction of the dye from similar suspensions by shaking with a non-miscible solvent such as one of the esters already mentioned.

How a solid body can act in the same way as a liquid solvent is not yet completely understood, or, to put the case more accurately, it is not yet seen clearly where the intimate details of the mechanism of this kind of solution begin to differ from the details of more conventional adsorption mechanisms. There are certain important quantitative criteria, the most cogent of which can be deduced from a thermodynamical reasoning similar to those which have been discussed earlier. Let us take a simple and classical example. Iodine is not very soluble in water, but very soluble in benzene. Benzene mixes only very slightly with water. Thus, if some benzene and some water are put together, a little iodine is added, and the whole shaken up extremely thoroughly and allowed to stand, the liquids separate eventually into two layers, each containing dissolved iodine. Then, within certain limits to be mentioned in a moment, it is found that, whatever the relative proportions of water, benzene, and iodine, the concentration of iodine in the water is always a fixed proportion of the concentration of iodine in benzene. In the accepted terminology, there is a constant partition ratio of iodine in the two-phase system. More iodine can be put in, more shaking and standing can take place, and still the *ratio* of concentrations remains unchanged, although, of course, the actual concentration in each layer will have gone up. This process can go on uninterruptedly until neither layer can take up any more iodine. Quite suddenly, each has become saturated. Any further addition of iodine results in a residue of iodine particles floating about in each layer, or packing themselves in a third layer between the two liquids. There are two important things to notice here. Since the constant distribution ratio persists up to the saturation of each of the liquids, it can be concluded that, for a solute X in the two solvents A and B, the following simple law will hold—

$$\text{Partition ratio} = \frac{\text{Concn. of X in A}}{\text{Concn. of X in B}} = \frac{\text{Solubility of X in A}}{\text{Solubility of X in B}} \qquad \text{(viii)}$$

If we like to plot the results as a curve of concentration in A against concentration in B, a straight line will result until saturation is reached. After this the curve will have to stop suddenly, because any further results, obtained by putting more X in, will be erratic and meaningless. The second point to notice is the suddenness of this stop. No other kind of distribution relation has it. In most others, the values tail off indefinitely.

How can this apply to the dyeing of cellulose acetate with, say, a Dispersol (ICI), a Cibacet (Ciba), or an S.R.A. (BrC) dye? Let it be said at once that there is some disagreement between the results and the interpretations of different workers in this field, because it is sometimes very difficult to get conditions which will allow the acetate dyeing to be strictly analogous to the partition experiments

just considered. Still, some claim to have established the parallel, and the following is the way the evidence goes. When cellulose acetate is dyed in a fairly dilute suspension of one of the disperse dyes, dye is taken into the fibre until an equilibrium is reached. With the more representative of these dyes the exhaustion is very high, reaching over 90%. Over a range of initial dyebath concentrations, it is found that the exhaustion remains constant up to the point where the cellulose acetate can take up no more dye. Any further addition of dye remains in the dyebath. Again drawing a curve of exhaustion against initial concentration, which will correspond to the partition curve described above, we obtain a straight line of constant slope which persists until saturation of the acetate rayon with the dye takes place. After this, any further dye remains in the form of microscopically visible particles in the bath, and the curve should make a sudden kink and continue parallel to the dyebath concentration axis. This is one of the testing points of the theory, and workers carrying out dyeing experiments have not always been able to find a kink of sufficient suddenness to convince them that an exact analogy with the two-liquid system exists. Quite recently Dr. Daruwalla, investigating the distribution of dye in a printing system, has found an almost exact reproduction of the theoretically predicted behaviour.

Because the dyes which are used in this system of dyeing have a very low solubility in water and a high saturation value in the fibre, the partition ratio, to which the exhaustion is proportional, is very high, so that the high exhaustion of the disperse dyes on cellulose acetate is explained. When, for the sake of convenience in certain dyeing and printing operations, an attempt is made to increase the solubility of the disperse dyes in water, by introducing a sulphonic acid group into the dye molecule as in the Solacet (ICI) range, the partition ratio swings markedly in a direction favourable to retention in the dyebath, so that the exhaustions found with this range of dyes are very much smaller than with the corresponding disperse dyes.

Before we leave this subject, a word may be said about recent developments in the dyeing and printing of acetate rayon and similar fibres. It has been seen that the cellulose acetate fibre cannot by itself absorb much water from an aqueous dyebath, and therefore cannot, it is believed, allow in molecules of many water-soluble dyes like direct and leuco vat dyes. Only when the fibre itself seems to be able to act positively as a dissolving agent, reducing the relatively coarse particles of the disperse dyes, do we appear to be able to carry out dyeing without the aid of secondary expedients. Still, it was believed that there was no fundamental difficulty in getting the cellulose acetate molecules to fix dyes of some of the other dyeing classes if once the dye could be got in. It is true that the hydroxyl groups have been diminished in number, and with them the capacity for hydrogen bond formation between dye and fibre. Still, there are some hydroxyl groups remaining, and these may be sufficient, for there is a big difference in dyeing properties between normal commercial acetate and the fully substituted triacetate. Thus there has arisen a large variety of the so called "carrier" or "solvent-swelling" procedures. In these a number of different inorganic and organic assistants, ranging from the inorganic thiocyanates to the organic solvents, may be added to the dyebath. The function of these agents is to cause increased swelling of the fibre, large enough to allow dye molecules to enter but not sufficient to cause disorganisation and loss in tensile strength. At the same time, it can be seen that many of the agents suggested could act, in the bulk, as solvents for many of the dyes being used, so that their presence in the dyebath, even in relatively small proportions, is calculated to discourage the aggregation of the dye molecules, and also perhaps to aid the dye to go easily into the fibre.

A variation on the same theme is the recent Thermosol process for Orlon. This is specially directed toward the type of fibre which can melt more or less sharply if the temperature is raised sufficiently high. This means, in fact, the fibres which cannot absorb water readily and do not swell in a dyebath of normal composition at temperatures below about 100°C. The implications are very interesting. We have seen that the reason why cellulose can swell readily in water is that it has a high proportion of hydroxyl groups to form hydrogen bonds with the water. This high proportion of hydrogen bonds also helps in the fixation of substantive dyes, but it ensures as well that the cellulose molecules stick very closely to each other. Thus, on being heated, the molecules of cellulose decompose before they separate sufficiently for the mass to become fluid. Wool and other forms of protein are cross-linked, often by covalencies, to such an extent that, although a certain amount of melting can occur, it is overtaken by decomposition. In a nylon molecule, on the other hand, there are two distinct parts. There are the amide parts, –NH·CO–, from which start the most powerful chemical forces which keep the molecules together; and there are the hydrocarbon parts —

$$-CH_2\cdot CH_2\cdot CH_2\cdot CH_2- \text{ and } -CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2-$$

over which intermolecular bonding is very weak, being of the same order as that which keeps the molecules of paraffin wax together. Thus nylon contains simultaneously what may be called "binding" groups alternating with "melting" groups —

$$\underset{\text{Binding}}{-CO\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH\cdot CO-}$$
Melting Binding

the binding groups are the ones to which we might look for the chemical fixation of substantive dyes such as acid and direct; while the melting groups would be those expected to impart solvent properties towards dyes of the disperse acetate-rayon class. When we are dealing with any dye towards which the fibre can exert a solvent action, it seems obvious that this action will be more pronounced, and will approach that of a

liquid solvent, as the freedom of the fibre molecules to move about is increased, i.e. as the fibre gets nearer and nearer to the molten condition. This is taken advantage of in the Thermosol process, where, after impregnation with a solution or a suspension of dye, the goods are raised to temperatures much above those of normal dyeing. There are two advantageous factors in such a process if it is carried out under the right conditions. The first, the assistance of the high temperature, has already been gone into. The second is an advantage encountered in all padding, steaming, and printing methods of applying dyes, for, in these methods, the volume of the effective dyebath at the moment when the dye is being transferred to the fibre is small, and the bath is thus very concentrated. In the competition for the dye between the water of the bath and the fibre-substance, it is obvious that the latter gains an increasing advantage as the amount of water present is cut down. Besides being common sense, this can also be proved by thermodynamic reasoning like that which has been discussed in the earlier part of this account. Those readers who have assimilated that part may like to make an attempt to prove it for themselves.

EFFECTS OF pH

Nylon is a useful example to illustrate many chemical dyeing principles. We have seen that the fibre molecules contain, neatly divided off from each other, groups like –NH– and $-NH_2$ on the one hand and groups like $[\cdot CH_2\cdot]_n$ on the other. The first type are groups at which electron exchanges can occur readily, and they are therefore able to be attached to groups in other molecules by hydrogen bonds, electrovalencies, and the like. In particular, they become ionised in acid solutions of low pH values, in which hydrogen ions H^+ abound. When these are moderately plentiful, say at about pH 3, the reaction—

$$-NH_2 + H^+ \longrightarrow -NH_3^+$$

takes place, and dye anions from acid or direct dyes can add on by electrovalencies as in salt formation—

$$-NH_3^+ + D^- \longrightarrow -NH_3D$$

With more strongly acid solutions, in a similar way, the >NH groups become $>NH_2^+$ and combine with dye ions to give $>NH_2D$, so that we have the acid dye adsorption going up, first moderately and then with a second big jump, as the dyebath passes from neutrality to strong acidity. Incidentally, it is not generally advisable to use the >NH groups in nylon for attaching dye, because the larger peptide group –CO·NH–, of which they form a part, is also the starting point of hydrogen bonds which attach one nylon molecule to another, thereby making a strong fibre. If they are interfered with, the strength of the fibre may drop in a spectacular fashion. Besides being dyed with acid dyes from acid baths, nylon can be dyed with disperse dyes, just as cellulose acetate itself, and here the pH of the dyebath has very little influence, so that it is obvious that the potentially basic groups are unlikely to be the means of attaching the molecules of dye to the fibre molecules, and that the "solvent" part of the nylon $[\cdot CH_2\cdot]_n$ is probably responsible. These two instances therefore represent the extremes of dyeing behaviour for the fibre, but there are interesting intermediate behaviours. For instance, with many acid dyes there is still some affinity even in neutral dyebaths, where the basic groups are in the unionised condition. When we were discussing Meggy's theory, attention was called to the presence of considerable "hydrocarbon" regions in the molecules of acid dyes, and it is probably through these regions that the "solvent" portions of the nylon molecule can bring about dye fixation.

References

[1] Boulton, J.S.D.C., **67**, 522 (1951).
[2] Marshall and Peters, J.S.D.C., **63**, 446 (1947).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Gas Fume Fault on Wool

Although faults due to burnt gas fumes are well known in the case of acetate rayon dyed with blue anthraquinonoid disperse dyes, similar faults on wool dyed with blue anthraquinonoid acid dyes do not appear to have been reported.

Recently, the writer investigated a fault on Lovat green, all-wool worsted trousers dyed with a level-dyeing mixture of azo yellow, azo red, and anthraquinonoid blue acid dyes. The trousers had been stacked in piles in a showroom heated by gas radiators, and where the cloth had been exposed to the atmosphere, i.e. at the outside of the piles, the colour had changed from dull blue-green to drab or khaki.

Experiments based on the Society's provisional gas-fume fading test [1] showed that blue anthraquinonoid acid dyes are very sensitive to nitrous fumes when exposed on filter paper, and that they are affected by prolonged exposure when dyed on wool. The greener types of blue appear to be more sensitive than the common Blue B type (*C.I.* 1054).

C. L. BIRD

DEPARTMENT OF COLOUR CHEMISTRY AND DYEING
THE UNIVERSITY
LEEDS 2

16th November 1954

[1] J.S.D.C., **64**, 134 (1948).

Notes

Meetings of Council and Committees
December 1954

Council— 8th

Finance— 8th

Publications— 21st

Colour Index Editorial Panel— 15th

Diplomas Executive Subcommittee— 4th

Symposium Papers Subcommittee— 3rd

Death

We regret to report the loss by death of Mr. J. T. Kidd.

Dyers Company Medal Committee

Mr. G. S. J. White has succeeded Mr. J. Boulton as Convener of the Worshipful Company of Dyers Research Medal Adjudication Committee.

London Lecture

The subject of the third London Lecture of the London Section will be *The Guilds of the City of London*. It will be given by Mr. P. E. Jones, LL.B., Deputy Keeper of the Records, Corporation of London, on Friday, 4th March 1955, at 7 p.m. The lecture will be held at the Waldorf Hotel, Aldwych.

Leeds Junior Branch

The officers and the committee for the current session are as follows—

Chairman	Dr. C. B. Stevens
Vice-chairman ...	Mr. C. L. Bird
Honorary Secretary ...	Mr. J. A. Felce
Committee	Mr. J. S. Bindra
	Mr. R. A. Brinkworth
	Mr. H. K. Partovi
	Mr. P. J. Smith
	Miss J. M. Wilson

The Society of Dyers and Colourists of Australia

ANNUAL REPORT 1953–1954

The Council has pleasure in presenting its sixth Annual Report. It is very gratifying to note that increased activity by all sections has occurred during the year ending 31st May 1954.

COUNCIL— The members of the Council met in Sydney on 27th July 1953 under the chairmanship of Mr. W. C. Castle, who was re-elected President. New appointments were— Mr. E. I. Noble as Honorary General Secretary, Mr. J. A. Fergusson as Honorary General Treasurer, and Mr. R. L. Runting as Editor of the Society's publications.

In appreciation of his services to the Society of Dyers and Colourists of Australia the honour of a life membership was conferred on Mr. L. P. Rendell.

The Council has concerned itself with modification of Rules and Bye-laws during the year.

FINANCES— The Honorary General Treasurer reports that all Sections are sound financially and that the total assets of the Society are £A909 12s. 1d.

MEMBERSHIP— In spite of some resignations, mostly due to change in occupation, the membership has increased during the year by 10 members. The Victorian Section has firmly applied the rules pertaining to membership, and other Sections are recommended to do likewise. The total membership is 358.

SECTIONS— All sections have arranged attractive programmes, and both lectures and such social functions as dinners and balls have been well attended.

The President's Golf Trophy was competed for by the Victorian, New South Wales, and Queensland Sections, resulting in a win for Mr. N. Gillies of the Victorian Section.

LIBRARIES— New additions to Sectional Libraries are reported. The services of the Honorary Librarians are much appreciated.

PUBLICATIONS— The Editor, Mr. R. L. Runting, has maintained the high standard of publications in the *Textile Journal of Australia*.

We are indebted to the authors of lectures and papers, who have permitted publication, and the kind co-operation of Mrs. A Mardell, Editress of the *Textile Journal of Australia*, is again appreciated.

It is with regret that the Council received the resignation of Mr. R. L. Runting as Editor. He has worked hard for the Society during the year, and continues to do so as Honorary Secretary of the Victorian Section.

During the year our President has visited all Sections again. He has attended the Annual Dinners of the Victorian and South Australian Sections. In Western Australia and in Geelong he has stimulated sufficient interest for residents to hold meetings, with the result that applications have been made for approval of the Council to form Sections of the Society in Western Australia and Geelong, Victoria. Mr. C. W. Cruickshank has been appointed Honorary Secretary (*pro tem.*) in Western Australia, and Mr. R. B. Sweeten Honorary Secretary (*pro tem.*) in Geelong, with Mr. J. Donaldson as Chairman (*pro tem.*).

OFFICERS AND COMMITTEES 1954–1955

President	G. A. Burns
Immediate Past President	W. C. Castle
Honorary General Secretary ...	E. I. Noble 12 Marne Street South Yarra, S.E.1 Victoria
Honorary General Treasurer	J. A. Fergusson
Publications Editor ...	D. L. Turner

SECTIONAL COMMITTEES

	VICTORIA	NEW SOUTH WALES	SOUTH AUSTRALIA	QUEENSLAND
Chairman	T. F. Hall	F. Foster	J. Burns	H. Tearle
Vice-chairman	W. J. Waldie	J. A. Eastwood	H. D. Bruce	W. H. Wright
Councillor	J. Brear	J. A. Eastwood	—	—
Honorary Secretary ...	R. L. Runting	H. C. Weinberg	G. D. Parsons	P. B. Hogg
Honorary Assistant Secretary	F. Brooke	—	A. G. Morris	W. Rogers
Honorary Treasurer ...	B. Firth	J. Lillicrop	H. D. Bruce	J. Lee

Your Council wishes to express to all members who have given their time in serving the Society its gratitude and appreciation for the excellent work done.

E. I. NOBLE
Honorary General Secretary

NEW SECTION OF S.D.C.A.

The Council of the Society of Dyers and Colourists of Australia has agreed to the formation of a new section of that Society in Western Australia (see above). A Subsection of the Victoria Section has been formed in Geelong.

The Worshipful Company of Dyers

Mr. R. P. Chambers has been elected Prime Warden. The Renter Warden is Mr. A. H. Brewin.

Worshipful Company of Feltmakers

The following officers have been elected—

Master	Sir Geoffry Christie-Miller, K.C.B., D.S.O., M.C., D.L.
Upper Warden ...	Mr. Ernest Bright Laycock, O.B.E.
Renter Warden ...	Lt.-Col. John Aylmer Christie-Miller, O.B.E., J.P.
Third Warden ...	Dr. Thomas Collyer Summers, M.B., B.S., F.R.C.S.
Fourth Warden ...	Sir Heneage Ogilvie, K.B.E., M.C., F.R.C.S.
Clerk	Mr. Sidney Alfred Williamson
Deputy Clerk ...	Mr. Ian David Wilson

An ancestor of Sir Geoffry Christie-Miller was Master of the Company in 1792–1793; and by a coincidence a descendant of Thomas Wontner, Master in the following year (1793–1794) was present as a member of the Court at Sir Geoffry's election, and it is hoped that in due course he will attain the Master's Chair.

B.S.I. Change of Address

The Manchester Office of the British Standards Institution has been moved to Corporation House, Market Street, Manchester 1 (entrance in New Brown Street). The new telephone number is BLAckfriars 4255, but the telegraphic address remains "Bristandin, Manchester".

The Society for Visiting Scientists

The Society for Visiting Scientists, established in the spring of 1944, when Britain had the honour of welcoming many scientists from overseas countries, seeks to be a focus for all scientists visiting the United Kingdom, and to put them in touch with British scientists and with one another. The society aims to provide and encourage an active exchange of scientific thought and discussion between scientists of the United Kingdom and scientists from overseas.

The house of the society provides a meeting place, a refectory, a bar, and some residential accommodation. In addition an information service is available for the use of all visiting scientists, so that any scientist arriving in this country can, if he wishes, proceed at once to the house and be given such advice and information as is available.

Among the society's activities is the holding of receptions in honour of groups of scientists visiting Britain, who thus have an opportunity of meeting at the house their British and overseas colleagues. Informal discussion meetings of general interest to scientists are organised; the society provides a forum for topics which are outside the scope of specialised scientific societies but which are of importance to scientists as a whole.

Scientists from all countries are welcomed at the society, which tries to assist its visitors in every way possible.

The annual subscription is three guineas, with an entrance fee of one guinea. Oversea postgraduate students in science holding research grants may become student associates, paying an annual membership fee of one guinea; they pay no entrance

fee. Other oversea members pay no annual subscription, but an entrance fee of five shillings.

Further particulars may be obtained from the Assistant Secretary, Society for Visiting Scientists Ltd., 5 Old Burlington Street London W.1.

International Conferences on Colour

An International Discussion on Problems of Colour Measurement, to be held at Heidelberg on 8th and 9th June 1955, will consider colour adaptation, colour vision, colour space, colour systems, and colour tolerances. Those who are thinking of attending are invited to send a preliminary notification to Herrn Prof. Dr. M. Richter, Fachnormenausschuss Farbe im Deutschen Normenausschuss, Berlin-Dahlem, Unter den Eichen, Germany. If they will inform also Dr. W. D. Wright, Imperial College, London S.W.7, he could look into the possibility of a party ticket.

The date of the meeting has been chosen to enable visitors to go on to the Congress of the International Commission on Illumination (C.I.E.) to be held in Zürich (Switzerland) during 13th–22nd June 1955. It had been intended to co-ordinate the Heidelberg discussion with the Third Congress of FATIPEC, concerned with problems of colour matching, to be held at Spa (Belgium) during 22nd–27th May 1955.

International Congress of Scientific Research in the Textile Industry

Brussels, 27th–29th June 1955

The programme will include three major lectures and a number of research papers. Inquiries should be addressed to the Secretary of the Congress, c/o Centre Scientifique et Technique de l'Industrie Textile Belge, 24 rue Montoyer, Brussels, Belgium.

Seventy-five Years of *The Dyer*

A special issue dated 12th November 1954 celebrated the seventy-fifth anniversary of the founding of *The Dyer, Textile Printer, Bleacher and Finisher* (the present title) in 1879. This had been preceded by *The Textile Colourist*, published for a year or two from 1876. The editorial recalls the part played by the *Dyer* in founding the Society, for the inaugural meeting in 1884 was convened by its manager, Mr. S. J. Sewell. Perhaps this special issue may be regarded as bearing witness to the continuing close relations between the *Dyer* and the Society, for the majority of the experts who review seventy-five years of development are leading members of the Society—H. A. Turner on the dyeing of cotton and cellulosic fibres, C. C. Wilcock on rayon dyeing, C. L. Bird on wool dyeing, A. W. Carpenter on hosiery dyeing, G. S. Hibbert on roller printing, F. L. Barrett and A. E. Stubbs on bleaching, C. S. Whewell on the finishing of woollen and worsted fabrics, K. A. Stott on cotton finishing, A. F. Kertess on textile chemicals, R. K. Fourness on dyes and dyeing methods for cellulose acetate, and P. Andrew on the dyeing and finishing of nylon stockings. The last two topics, of course, were unknown in 1879.

We congratulate the *Dyer* on its seventy-five years of service to the tinctorial industries and on its special issue, and wish it many more years of interesting publication.

International Symposium on Macromolecular Chemistry

It has become the custom for an International Symposium on Macromolecular Chemistry, sponsored by the Commission of Macromolecular Chemistry of the International Union of Pure and Applied Chemistry, to be held annually in a different country each year, and in 1954 the choice fell on Italy. Meetings were held between September 26th and October 3rd in both Milan and Turin, and altogether some eighty papers were presented and 250 chemists and physicists attended the conference. It is a sign of the times that seventeen papers dealt with fibre-forming polymers, with the emphasis on man-made fibres, and many representatives of chemical firms which manufacture synthetic fibres attended the conference.

The papers presented at the meetings were of a high standard, almost invariably dealing with truly new work and not, as is often the case at similar conferences, with descriptions of work that has already been published. It would be impossible in the space at the Reporter's disposal to give an account of all the papers that have some bearing on fibres, but those discussed below are believed to be the most significant.

Opening the Milan meeting, Professor H. Mark, the Director of the Polymer Research Institute of Brooklyn, gave a most stimulating account of *New Rubbers, Plastics, and Fibres*, indicating the main trends of research at present. In the field of synthetic fibres, the main stimulus is the quest for improved dyeing properties and higher moisture absorptions, and here the work of Dr. R. Hill and his collaborators at I.C.I. Ltd. on the formation of block copolymers of polyethylene terephthalate and polyoxyethylene was most important. Another significant development was the mechanical texturing of continuous-filament yarns (e.g. nylon) so that they have a softer and warmer handle. The Teslan nylon yarns manufactured by du Pont in this way can be made into fabrics with a handle resembling that of cotton. The same organisation has recently introduced another new fibre, Teflon, made from polytetrafluoroethylene. This polymer cannot be dissolved or melt-spun, and fibres are formed by techniques similar to those used in the processing of metals. In view of its outstanding thermal and chemical resistance, it must find numerous industrial applications, e.g. dye-bags.

The degree of dispersion of viscose spinning solutions has been a matter of controversy, and two papers had some bearing on this problem. K. Hess reported that X-ray examinations indicated that

the xanthate in spinning solutions is dispersed not to molecules but to layers of molecules. On the other hand, O. Kratky and G. Porod have found that solutions in which cellulose is known to be molecularly dispersed can be concentrated and then spun into fibres in which the size of the crystallites is almost exactly the same as in fibres spun from normal "solutions", in which micelles or crystallites occur. It is thus shown that crystallisation from a true molecular solution can take place, although, of course, this does not prove that such a process is of any importance under normal spinning conditions.

Another topic which is attracting much current attention is the long-range periodicity exhibited by many fibres. Using the technique of staining fibres with iodine, K. Hess has been able to obtain electron micrographs of cellulose and polyvinyl alcohol fibres which exhibit extraordinarily clearly periodicities of about 150 and 700 A., which are attributed to the regular alternation of ordered and unordered regions of the fibre. A most careful X-ray determination of the crystallinity of polyvinyl alcohol fibres was reported by Professor I. Sakurada. The crystallinity can be increased by increasingly severe thermal treatments, exposure to a temperature of 200°C. for 2 min. being sufficient to produce a degree of crystallinity of 54% and to make the fibre completely insoluble in water at room temperature.

A most novel and intriguing phenomenon was described in a paper by T. G. Majury and H. J. Wellard of the British Rayon Research Association. Films of secondary cellulose acetate in which molecular orientation has been induced by stretching will, when subjected to aqueous solutions of certain swelling agents such as phenol, ethanol, or dioxan, undergo further elongation, and not, as might have been expected, contraction, without application of a load. The effect may be large, a spontaneous extension of 300% following an initial stretch of only 20%. It has also been found possible to prepare highly crystalline secondary cellulose acetate. No satisfactory explanation of this curious behaviour has yet been offered, and it certainly induced much cogitation in those who heard of it at the meeting.

A comprehensive examination of the crystallisation of 6,6-nylon by L. B. Morgan and his collaborators revealed the extraordinary sensitivity of the fine structure or morphology of this polymer to the conditions of melting and processing.

Finally, there were several excellent papers dealing with the physical properties of fibre-forming polymers, but unfortunately no account of these can be given here. L. V

Fibres from Mixed Polymers

It is reported that fibres have been prepared by spinning a mixture of polymers from a common solvent. Not all polymers soluble in the same solvent are compatible, however, and precipitation or the formation of immiscible liquid layers may result on mixing. The hydrophobic polyacrylonitrile and hydrophilic cellulose acetate are compatible, and fibres containing 20–95% of the former have been spun from dimethylformamide solution. The properties of the fibres vary directly with composition. A particular advantage is improved dyeing with acetate-rayon dyes in proportion to the amount of cellulose acetate in the fibre. The results suggest a means of overcoming the difficulties associated with the hydrophobic nature of fibres such as polyacrylonitrile. The work is being carried out at the Textile Research Institute under the direction of H. J. White — *Ind. Eng. Chem.*, **46**, 18A–20A (Oct. 1954). W. K. R.

Phrilon becomes Perlon

The Phrix Gesellschaft m.b.H. of Hamburg has joined the Perlon-Warenzeichenverband e.V. of Frankfurt-am-Main. The product previously known as "Phrilon" will in future be marketed as *Perlon*.

New Books and Publications

Matthews'
Textile Fibers
Their Physical, Microscopic, and Chemical Properties

Edited by H. R. Mauersberger. 6th edition 1954. Pp. x + 1283. New York: John Wiley & Sons Inc. Price, $16.50 or 132s. 0d.

There can be few practising textile technologists who have not known "Matthews" all their active life, and few textile students over the last fifty years who are not familiar to a greater or less extent with its contents.

The last edition of which J. M. Matthews was the sole editor was the fourth, published in 1924, and to the outsider it almost appeared that this was to be the end. It was an event of some importance to textile students, therefore, when, twenty-three years later, a new edition, the fifth, appeared under the editorship of H. R. Mauersberger, supported by a team of American authorities on the different aspects of textiles.

A new edition is now issued after only seven years, but this is obviously called for in view of the appearance of a wide range of man-made fibres, and indeed this is stated to be the main reason for its introduction at this time. As before, it has been compiled under the editorship of H. R. Mauersberger by a team of American authorities.

It should be appreciated that "Matthews" deals only with fibres and yarns, but this it does in an effective manner, selecting from the enormous range of information available. Each chapter

contains references to the original source of information, thus enabling the reader to enquire more fully into those subjects in which he is particularly interested.

The text has been rearranged somewhat into 22 chapters, which are rather fewer than in the previous edition, but the total number of pages is now 1283, an increase of some 150, and the book weighs almost 5 lb.

As would be expected, the new edition covers not only the newer fibres but also the application of some of the newer chemical and physical techniques applicable to all fibres; mention may be made of a chapter on the X-ray diagrams of natural and synthetic fibres and a revision of that on static electricity. Nevertheless, from the nature of the publication it is impossible for it to be completely up to date, and one may quote the omission of Orlon 42 in this connection.

Matthews' Textile Fibers will continue to serve its useful purpose as a textbook for students and as a standby for the experienced technologist, and the new edition will be welcomed throughout the textile industries. P. W. CUNLIFFE

Rayon Technology (including Acetate)

Handbook for Textile Mills

Prepared by the Textile Research Department, American Viscose Corpn. 2nd edition 1953. Pp. vii + 344. New York: McGraw-Hill Book Co. Inc. Price, $7.00.

In this age of new fibres it is important for the textile technologist to remember that rayon is still by far the most widely used of the man-made fibres and that new techniques in its manipulation are continually being developed. This handbook of methods and suggestions for processing rayon on different types of machinery is designed to help those who already have a knowledge of conventional textile processes, and it embodies the combined technical experience of the staff of the Textile Research Department of the American Viscose Corporation. The second edition has been enlarged to include the technology of acetate rayon as well as viscose rayon, and in addition the various sections on yarn processing, weaving, knitting, dyeing, and finishing have been revised to incorporate the latest techniques: e.g. the production of yarns by blending viscose rayon with acetate rayon, cotton, and wool is discussed in some detail with special reference to the best type of lubricant for each blend.

Two chapters have been added, on Industrial Applications and Textile Chemicals, but these do not maintain the standard of the rest of the book, and they seem to indicate a change in editorial policy. In view of the widespread use of rayon for special purposes the chapter on Industrial Applications is of necessity very sketchy, and deals with a few selected topics such as the spinning of asbestos yarns, bonded-fibre fabrics, viscose rayon flock, and mechanical rubber goods. The section on Textile Chemicals is even more limited in scope, and describes the products developed for textile processing by the American Viscose Corporation. Apart from these two chapters, the book is well written. It should be of interest to textile technologists in this country, as it contains the "know-how" of one section of American industry.

W. G. CAMERON

Guide to Pigments and to Varnish and Lacquer Constituents

By J. H. Martin and W. M. Morgans. Pp. 127. London: Leonard Hill Ltd. 1954. Price, 12s. 6d.

This volume presents yet another glossary of names of compounds and terms used in the pigment, paint, oil, varnish, and printing ink industries, the first 54 pages dealing with "Pigments and Related Products" and the remainder with "Varnish and Lacquer Constituents".

The blurb implies that such a glossary has become desirable in view of the increasing complexity of the manufacture of resins, media, and pigments, and states: "The authors have intended to include trade expressions currently in use and have tried to achieve a compromise between the terms of the art and of the science. By this means it is hoped that this work will be of assistance both to the established orthodox paint manufacturer and to the newly recruited scientist and technologist".

The authors of books intended specifically as works of reference should recognise their special responsibility, not only for accuracy of statement, but for the provision of something more helpful than mere definition. The pigments section of this volume, in particular, is very open to this criticism. The majority of the organic pigments listed are simply defined, no indication whatever being given of their properties. It would seem to be far more useful that the paint technologist should know that Hansa-type yellows bleed badly, and hence are useless, in cellulose solvents, than simply that they are produced by "coupling diazotised bases with acetoacetanilide or its substitution products". Similar indications in respect of the organic pigment reds, maroons, etc. would obviously be of real value to the intended reader: e.g. that C Lake Reds are yellowish-toned reds, having varying degrees of bronze, good light fastness, brilliance, and strength; or that D Lake Red has good tone and strength, but is unstable in the presence of cobalt driers, becoming darker and less brilliant. Extension of the statements made in some cases would avoid misleading impressions: e.g. the statement that Fanal, Brillfast, or Consol Colours are fast to light should be qualified to read that, although they are relatively fast to light as compared with earlier lakes of equal brilliance, they are not sufficiently fast for use in exterior paints, but are extensively used in printing inks.

The space required for such amplification could readily, and very profitably, be obtained by the elimination of far too much and quite unnecessary cross-referencing; e.g. Dry Ice—Ice, dry—Chrome, zinc—Zinc, chrome (often with full definition in each case), and many common commercial chemicals and self-evident or commonplace entries, e.g. Soda, washing—Nitric acid—

Caustic soda, etc.; Drying, Rust, Sand, Sieve, etc.

As a book of reference, the value of both sections would have been greatly enhanced by the inclusion of references (separately tabulated if necessary) to the relevant British Standard Specifications, which apply to almost every pigment entry, to linseed oil, volatile thinners and solvents, and to the determination of fastness to light. Similarly, the relevant Statutory Orders and British Specification detailing the determination of "soluble lead" might well be quoted.

In general, the pigment section gives the impression of an attempt to cover far too wide a field in a limited compass, with the many omissions and unnecessary inclusions which are an inevitable consequence.

In contrast to the pigment section, the Varnish and Lacquer glossary gives much better guidance to the properties and general uses of the individual constituents, and the unnecessary cross-referencing has been eliminated almost entirely.

The whole volume shows some evidence of careless or non-technical proofreading, which is most undesirable in a "glossary" : e.g. p. 18 refers to the "combustion" of carbonate white lead instead of *composition*; on p. 34 lead nitrate is given water of crystallisation which does not exist; p. 71 refers to the "quality" of catalysts and reactants instead of *quantity*; p. 123 states that ultraviolet light has a "sharper" wavelength than visible violet light.

With careful revision, addition, and rearrangement, especially in the "pigment" entries, this book could become a useful work of reference to those for whom it was originally intended.

G. E. Hillier

An Advanced Treatise on Physical Chemistry

Volume Four

Physico-Chemical Optics

By J. R. Partington. Pp. xl + 688. London: Longmans, Green & Co. 1953. Price, 80s. 0d.

This book contains a comprehensive account of physical optics. The range of subjects treated bears a family resemblance to those in Wood's old classic on this subject, which has been reprinted so many times. Besides the resemblance there are many differences, because the book under review is concerned with chemical as well as physical optics. For example, optical activity receives a very full treatment in Professor Partington's book, where generally the style is exhaustive and mathematical.

Despite the large size of the book, the argument frequently depends on derivations contained in one or other of the three earlier volumes. To be equipped to follow the argument through requires the expenditure of the not inconsiderable sum of £14 4s. 0d. for the set of books to date. In making cross-references a special system is used. The section, the subsection, and the paragraph but not the volume are indicated by roman and arabic numerals and a letter. This system may appear strange at first. It was probably a greater facility to the author than it will be to the reader.

From the early work of Naegeli onwards optical methods have proved of great value in studying fibre structure. In recent years Frey-Wyssling, Hermans, Preston, Bunn, and Morgan amongst others have applied optical methods to the solution of physicochemical problems in fibre and macromolecular structures generally. Many other examples could be chosen, e.g. the use of light scattering in studying solutions of macromolecules. In these fields of work the present book will be found a most useful source book of literature references, of which it contains more than ten thousand. But the book is more than a source book, for it contains very full discussions of the various aspects of the subject. Wherever possible, the arguments are expressed mathematically, which means that only those readers with a good mathematical equipment will be able to derive much benefit from consulting it.

The book can be strongly recommended to all advanced workers.

J. M. Preston

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Principles governing the Efficiency of a Padding Mangle. H. Potter. J.S.D.C., **71**, 20–26 (Jan. 1955).

A simple theoretical discussion shows how the take-up of liquor in a fabric after passing through a squeeze mangle depends upon the distance of closest approach of the bowl surfaces. The mathematical relationship between this distance, the physical characteristics of the mangle, and the compressional characteristics of the fabric is worked out for an ideal case. How the final take-up in any practical case might depend upon other important factors is also considered. AUTHOR

Cylinder Drying of Materials. L. Walter. *Textile Weekly*, **54**, 1480, 1482, 1484 (5 Nov. 1954).

An account of the mechanism of contact drying of fabrics and suggestions for obtaining maximum efficiency. Automatic temperature control of the cylinders is discussed. C. O. C.

PATENTS

Thickening of Emulsions or Suspensions. Maatschappij voor Kolenbewerking Stamicarbon. *BP* 716,594

Apparatus for thickening a suspension or emulsion and obtaining one with a certain minimum or maximum concentration of suspended or emulsified matter comprises one or more hydrocyclones which are constructed to take advantage of the fact that the angle of the discharge cone from the discharge aperture is directly determined by the viscosity of the discharging liquid rather than by that of the feed. By adjusting the dimensions and separation of the discharge and collecting cones a fractionation system is set up whereby over-weak or over-strong concentrations are recycled. J. W. B.

Furnaces for Making Carbon Black. Sutcliffe Speakman & Co. *BP* 717,672

Furnace for Making Carbon Black. Columbian Carbon Co. *USP* 2,656,254

Pelleting Chain Structure Carbon Black. Phillips Petroleum Co. *USP* 2,656,257

Apparatus for Producing Carbon Black by the Explosion Process. H. L. Ammann. *USP* 2,658,821

Wet Treatment of a Continuous Tow of Filaments. Courtaulds. *BP* 717,258

Modification of *BP* 618,925 (J.S.D.C., **65**, 376 (1949)), the buoyancy of the tow being improved by introducing one or more streams of air or other gas into the liquor beneath the accumulated tow so that the bubbles of the gas rise through the liquor into the tow. C. O. C.

Wet Processing of Yarns. Hampton Machine Co. *USP* 2,657,565

Each end is separately treated as it travels from a supply package to a repackaging device. Efficient treatment is obtained at speeds of 400 yd. per min. or more. C. O. C.

Drying Wound Textile Packages. American Viscose Corpn. *USP* 2,657,472

A method of drying rayon cakes that is adaptable to conventional convection drying equipment. C. O. C.

Preheating Goods for Molten-metal Dyeing Process. Standfast Dyers & Printers. *BP* 716,708

Modification of *BP* 681,983 (J.S.D.C., **69**, 36 (1953)). The goods are preheated before passing into the dye liquor so that they are never at $< 80°$C. while in the liquor. Excess liquor is removed from the goods immediately they leave the bath, e.g. by use of a vibrator, beater or doctor, and then passed into an atmosphere of steam. This gives uniform dyeings very quickly. C. O. C.

Pin Chains and Guides for Tenters. John Dalglish & Sons. *BP* 717,670

The advantage of closeness of nozzles to the fabric is obtained with a comparatively normal nozzle (and tenter) arrangement. C. O. C.

Screen and Stencil Printing. Roto-Matic Screen Printer. *USP* 2,651,257

A screen or stencil printing machine in which the blanket moves at a uniform linear speed, particularly during drying and application of the fabric to be printed. There is little wear on the blanket. C. O. C.

Stencil and Screen Printing Apparatus. Roto-Matic Screen Printer. *USP* 2,651,988

A power driven semi-automatic screen printing machine in which the length of stroke of the scraper blade is easily varied. C. O. C.

Electrically Heated Rollers for processing Plastic Materials, Textiles, etc. ICI. *BP* 716,863

A calender bowl's surface is electrically heated in such a manner that there is accurate control over the temperature and only a small time lag in adjustment from one temperature to another. C. O. C.

Drum Washing, Dry Cleaning or Garment Dyeing Machines. Isaac Braithwaite & Son, Engineers. *BP* 717,974

Between the outer casing and the drum there is an imperforate cylinder having a peripheral gap or a cylinder having a ring or rings of perforations extending over a small part of the cylinder's length. Perforated lifters carried by this cylinder project through slots in the drum. Scoops carried by the cylinder co-act with the lifters to direct the liquid in the lower portion of the outer casing to the lifters as the assembly rotates in the outer casing. This machine has the advantages of the machine described in *BP* 640,974 (J.S.D.C., **66**, 593 (1953)) while giving quicker rinsing and washing. C. O. C.

Vacuum Spotting Board. W. M. Cissell Manufacturing Co. *USP* 2,657,566

A sleeve board swings parallel to the main spotting board. Swinging the sleeve board operates a valve which disconnects the suction line of one board while simultaneously connecting the suction line of the other board. C. O. C.

Laundry Press. G. E. Tidbury. *BP* 718,432

Rug Scouring Apparatus. Proctor & Schwartz. *USP* 2,656,701

The rugs are held on to an endless conveyor by means of pins and while so held are scrubbed on one side and rinsed. They are then transferred to a conveyor where they are scrubbed on the other side and rinsed. This gives speedy and uniform cleansing of the rugs and prevents shrinkage.

USP 2,657,045

A similar machine employing only one conveyor on which the rugs are scrubbed on both sides. C. O. C.

Electrostatic Coating. Ransburg Electro-Coating Corpn. *USP* 2,658,009

A secondary stabilising field adjacent to the electrostatic spray atomising, projecting and depositing field, stabilises the jet produced by the latter both directionally and in respect to shape. This results in more sharply defined patterns. C. O. C.

Paper Coating Machine. E. J. Worden. *USP* 2,653,566

A machine in which the deckle edge of the paper is maintained and in which the rolls do not become clogged with adhesive at the edges of the paper. C. O. C.

Charging Apparatus for Feather Treating Machines. L. H. Lorch, AG Maschinenfabrik. *BP* 717,991

Automatic, continuous and uniform charging of raw feathers into cleaning etc. machines, is described. C. O. C.

Compressional Wave Energy in the Upper Sonic and Supersonic Range for Washing Textiles (VII p. 64).

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

PATENTS

Sulphated Acylalkanolamides—Detergents and Emulsifying Agents. Dutton & Reinisch. *BP* 717,903

The products obtained by treating compounds of formula—

$$R^1{\cdot}CO{\cdot}NR^2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

(R^1 = sat. or unsat. Alk of 3–19C and may contain a homocyclic ring substituent and/or non-carbon substituents; R^2 = H or Alk of $<$ 4C; the CH_2 groups may be substituted by one or more Alk together containing $<$ 5C) with H_2SO_4 in presence of acetic or propionic acid or anhydride have useful detergent and emulsifying properties. C. O. C.

Stabilised Starch Derivatives. National Starch Products. *USP* 2,654,736

The products obtained by treating starch with the inner esters of β-hydroxy aliphatic acids yield solutions which remain clear and of constant viscosity for prolonged periods. C. O. C.

Starch Pastes. Springs Cotton Mills. *BP* 718,465

The starch is formed into an aqueous paste in a vat and from there is continuously circulated by a pump through a chamber where it is heated by live steam. This enables a much larger volume of steam to be used than is possible with conventional kettles and so enables the processing time to be reduced by two-thirds. C. O. C.

Zirconium Salts of Water-soluble Carboxyalkyl Cellulose as Textile Sizes. Hercules Powder Co. *USP* 2,650,887

Permanent sizing of improved resistance to laundering acids and alkalis is produced by treating first with a water-soluble carboxyalkyl cellulose derivative, then with a zirconium salt and finally giving a mild alkaline wash. C. O. C.

Modifying and Converting Starch. Corn Products Refining Co. *BP* 718,174

Starch of from 1% to 30% moisture content is mixed with aluminium chloride hexahydrate at 20–105°c. and pH 2·8–3·4 and 30 min. later the aqueous slurry is treated with an enzyme, e.g. a saccharifying or a liquefying enzyme. The converted starch is roll dried to give a cold-water dispersible product of intrinsic viscosity at 35°c. of 0·15–0·30 in N-KOH. 0·1 to 0·2% by weight of calcium carbonate (based on the weight of starch) and sufficient alkali e.g. gaseous ammonia, to bring the pH to 5·5–7·5 may be added, followed by a liquefying enzyme to yield a converted 1 : 2 to 1 : 3 starch suspension having a Dudley viscosity of 60–150 sec. Conversion may be continued until the liquor has a total fermentables content of 70%, based on dry solids, and the starch may be converted in presence of clay, to prepare a paper coating composition. S. V. S.

Homogeneous Aqueous Colloidal Dispersion of Silica and a Hydrous Oxide of Zinc, Aluminium, Tin or Niobium. DuP. *USP* 2,657,183

An aqueous solution of an alkali metal silicate and an alkali metal zincate, aluminate, stannate or niobate is passed through an acid-treated ion-exchange material. The product is a colloidal dispersion of the mixed oxides. It may be used for imparting wet-strength to paper, for slip resistant finishes on textiles and for improving the water-resistance of hydroxylic polymers. C. O. C.

Imino-dicarboxylic Acids—Auxiliary Agents and Dyes forming Metal Complexes. Ciba. *BP* 718,509

Compounds of formula—

$$(HO)_x{-}R{-}\left[CH_2{\cdot}N\begin{matrix}C_yH_{2y}{\cdot}COOH\\C_yH_{2y}{\cdot}COOH\end{matrix}\right]_y$$

(R = subst. or unsubst. aromatic residue of the benzene series; $x = 1$ or 2; $y < 5$; $z < 4$; at least one of the

$$CH_2{\cdot}N\begin{matrix}C_zH_{2z}COOH\\C_zH_{2z}COOH\end{matrix}$$

groups is in *ortho* position to a hydroxyl group) or functional derivatives of such acids, are able to form complex metal compounds with various metal ions. Compounds obtained from phenols can be used for inhibiting formation of or dissolving lime soaps. Compounds containing higher alkyl residues, e.g. butyl or amyl, are suitable as mercerising assistants. The copper, zinc and mercury salts of some compounds can be used as rotproofing agents. Those compounds which are dyes are best used as their copper or chromium complexes. C. O. C.

Stripping Agents for Wool Dyes, on Wool, Silk, Nylon, or Casein Fibres, etc. Ciba. *BP* 718,010

The products obtained by heating 4 mol. of an $\alpha\beta$-alkylene oxide with 1 mol. of an organic compound containing at least one basic primary or secondary amino group or containing a basic tertiary amino group and an alcoholic hydroxyl group or a product obtained by introducing polyglycol ether chains into the above amines, or the salts or quaternary ammonium salts of the above products, used in acid, neutral or alkaline liquors are excellent stripping agents for wool dyes on nitrogenous fibres. C. O. C.

***N*-Acylamino Mercaptans—Agents for Setting Proteinaceous Materials.** Basf. *BP* 718,063

The products obtained by treating ethyleneimine with compounds of formula R·CO·SH $\rightleftharpoons$ R·CS·OH (R = methyl or phenyl) are used for permanently setting proteinaceous fibrous materials. Thus wool impregnated with a 0·1–10·0% aqueous solution of such a product and then dried retains the form which it had or into which it was brought during treatment, e.g. wool fabric may be permanently pleated or embossed. C. O. C.

Stable Liquid Urea–Formaldehyde Condensates. Allied Chemical & Dye Corpn. *USP* 2,652,377

Stable high strength solutions of urea–formaldehyde condensates are produced by dispersing urea in the solutions using 1 mol. urea for each 4·4–7·3 mol. HCHO in the condensate after bringing to pH 8·8–9·5. C. O. C.

Catalysts for Hardening Thermosetting Aminoplasts and the like. Ciba. *BP* 716,952

The products obtained by treating conc. aq. boric acid with conc. aq. salts of an acid of dissociation constant $\leqslant 2{\cdot}1 \times 10^{-4}$ with a metal of Group I or II of at. wt. not greater than that of Ca, are excellent catalysts for use in resin solutions used for crease resisting, etc. They have the advantage that treatment of dyed materials with resin soln. containing these catalysts has either no or negligible effect on the light fastness. C. O. C.

Antistatic Agents for Vinyl Fibres and Resins. American Cyanamid Co. *USP* 2,652,348

Compounds of formula—

$$ROOC{\cdot}CH_2CH\begin{matrix}COOGn\\SO_3Gn\end{matrix}$$

(R = long chain aliphatic radical; Gn = guanidine, lower alkyl guanidines, phenyl guanidines, alkylol guanidines, guanylurea, biguanide or phenyl biguanides), e.g. octadecyldiguanidine sulphosuccinate, are excellent antistatic agents for use on vinyl fibres and resins. C. O. C.

Antistatic Size for Polyethylene. DuP. *USP* 2,653,113

An extremely dil. aqueous composition containing dispersed polyvinyl acetate, a mixture of compounds of formula—

$$(AlkO)_x{\cdot}PO{\cdot}[O(NX)H]_y$$

(Alk = primary satd. aliphatic hydrocarbon radical of $>$ 5C; NX = mono-, di- or triethanolamine, monoethanolmonomethylamine, ethanoldimethylamine, diethanolmethylamine and morpholine; $x = 1$ or 2; $y = 3{-}x$) and, if desired, NaCl, is an excellent antistatic size for polyethylene. C. O. C.

Antistatic Agent for Vinyl Resins and Fibres. American Cyanamid Co. *USP* 2,654,678

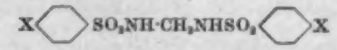
Compounds of formula—

$$HN{:}CNH_2{\cdot}NH_2{\cdot}HO_3S{\cdot}CH(CH_2{\cdot}CONHR){\cdot}COOH{\cdot}NH_2{\cdot}CNH_2{:}NH$$

(R = Alk of > 11C), e.g. *N*-monohexadecyl diguanidinium sulphosuccinamate, are antistatic agents for use with vinyl resins and fibres. C. O. C.

Mothproofing Agent. Merck & Co. *USP* 2,654,677

Compounds of formula—



(X = Cl or Br) are insoluble in water but soluble in most common organic solvents. They are used as mothproofing agents e.g. presence of 0·25% of bis(*p*-chloro (or -bromo) benzene sulphonyl) methylene diamine confers immunity against the attacks of clothes moths or black carpet beetles. C. O. C.

Insect Repellents. U.S. Secretary of the Army. *USP* 2,653,894

Fabric treated with diols of formula—

$$A(OH)_2$$

(A = unsat. Alk of 10–14C, an open chain of 8–10C, and contains a double or triple C to C bond; the OH groups are alcoholic and attached to different C atoms on either side of the double bond) e.g. 2:5:7-trimethyl-3-octenediol-2:5, is repellent to mosquitoes, etc.

USP 2,653,895

Compounds of formula—

$$YCH_2COOB$$

(B = open chain or an alicyclic ring substituent of < 7C; Y = an amino group have attached to the N atom a satd. or unsatd. cyclic substitute of < 7C by means of a CH_2 group), e.g. butyl ester of *N*-benzyl glycine, are used. C. O. C.

4-Octyl and Nonylpyridines as Fungicides. Reilly Tar & Chemical Corpn. *USP* 2,658,850

4-Octyl- and 4-nonylpyridines are very effective fungicides suitable for application to textiles and leather. C. O. C.

Solvents for Polyacrylonitrile. Chemstrand Corpn. *USP* 2,654,721

A mixture of *NN*-dimethylacetamide, acetic acid (2–8% by wt.) and sulphuric or sulphamic acid (0·05–0·25%) dissolves polymers containing < 80% acrylonitrile. The solutions have a low enough viscosity to allow them to be spun by commercial methods. C. O. C.

Solvents for Polyacrylonitrile. American Cyanamid Co. *BP* 717,972

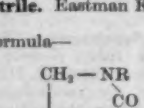
The polymer is dispersed in an aqueous solution of a salt yielding highly hydrated ions, e.g. a thiocyanate, the solution being of such strength that the polymer does not dissolve, and then adding sufficient of the salt to bring the solution to a strength at which it dissolves the polymer. This enables the time of dissolution to be halved. C. O. C.

Aqueous Nitromethane as Solvent for Acrylonitrile Polymers. DuP. *USP* 2,658,879

A 55–96% aqueous solution of nitromethane dissolves polymers containing < 85% by wt. of acrylonitrile and is readily completely removed from the polymer. C. O. C.

***N*-Substituted Ethylene Carbamate— Solvent for Polyacrylonitrile.** Eastman Kodak Co. *USP* 2,656,328

Compounds of formula—



(R = Alk, hydroxyalkyl, *cyclo*alkyl, cyano or subst. or unsubst. Ar) are good solvents for acrylonitrile polymers or copolymers. C. O. C.

Solvents for Polyacrylonitrile. Chemstrand Corpn. *USP* 2,656,329

Mixtures of diethyl phosphite and *NN*-dimethylacetamide or *NN*-diethylformamide are excellent solvents for acrylonitrile copolymers. C. O. C.

Solvents for Grafted Acrylonitrile Polymers. ICI. *BP* 718,137

Ethylene carbonate–water mixtures are excellent solvents for grafted acrylonitrile polymers. Preferably there is > 60% by weight of ethylene carbonate in the mixture. C. O. C.

Radio-active Decontaminants. F. C. Bersworth. *BP* 716,574

A composition comprising a mixture of (mostly) the Ca complex of an alkali metal, ammonium or amine salt of an aliphatic polyamino polycarboxylic acid, together with a minor proportion of the salt itself, e.g. disodium-calcium salt complex of ethylene diamine tetraacetic acid with tetrasodium ethylene diamine tetraacetate, functions as a radioactive decontaminant by virtue of Ca replacement, under alkaline conditions, by almost any metal except alkali metals. Even radioactive Ca 45 displaces Ca 40 to an equilibrium. It can be used on skin or clothing, e.g. in aqueous 5–20% solution plus a little ordinary soap. J. W. B.

Plasticisers for Cellulose Nitrate Coating Compositions. Atlas Powder Co. *BP* 718,678

The phenoxyethyl and phenoxypropyl esters of oleic acid or of tall oil are good plasticisers for cellulose nitrate coating compositions. C. O. C.

Driers. Monsanto. *USP* 2,658,003

The polyvalent drier metal salts of monoalkyl esters of di(or tri-)*iso*butenylsuccinic acid (Alk of 1–4C) are faster drying than conventional driers and are exceptionally stable against oxidation. Preferably the Pb, Co, Mn and Zn salts are used. C. O. C.

Rendering Dyes, Azoic Coupling Components and other Solids Water-dispersible (IV p. 61).

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Nitryl Fluoride as a Nitrating Agent. G. Hetherington and P. L. Robinson. *J.C.S.*, 3512–3514 (Oct. 1954).

Nitryl fluoride, prepared by passing a stream of F_2 diluted with N_2 over well dried $NaNO_3$, is shown to be an active nitrating agent, although it is somewhat selective in its attack, leaving such deactivated aromatic compounds as nitrobenzene, benzoic acid, and benzaldehyde largely unchanged. With substances of intermediate reactivity, nitration is rapid and smooth, and similar to that of mixed acids. Highly reactive materials, e.g. aniline, anisole, and quinoline, are converted immediately into intractable tars. The results indicate that nitryl fluoride stands higher than nitryl chloride in the series of nitrating agents of the type $X{\cdot}NO_2$, in which the nitrating power increases with the electron-accepting quality of X. H. H. H.

Hydrogen Transfer. VII— Metal-catalysed Transfer-hydrogenation of Nitro Compounds. E. A. Braude, R. P. Linstead, and K. R. H. Wooldridge. *J.C.S.*, 3586–3595 (Oct. 1954).

Transfer-hydrogenation, with *cyclo*hexene as hydrogen donor and Pd as catalyst, provides a convenient general method for the conversion of aliphatic and aromatic nitro compounds into primary amines. In the presence of more than one functional group, transfer-hydrogenation is often remarkably selective, affording higher yields than direct catalytic hydrogenation or other reduction methods. A mechanism is proposed which accounts for the difference in specificity in terms of surface-stereochemical effects. H. H. H.

Hydrogen Transfer. VIII— Metal-catalysed Transfer-hydrogenation of Miscellaneous Acceptors. E. A. Braude, R. P. Linstead, P. W. D. Mitchell, and K. R. H. Wooldridge. *J.C.S.*, 3595–3598 (Oct. 1954).

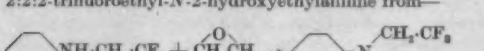
The Pd-catalysed transfer-hydrogenation of miscellaneous acceptors of *cyclo*hexene is investigated. Not only

ethylenic, acetylenic, and nitro groups (cf. preceding abstract), but also azomethine, azo, and azoxy groups and some halogen compounds, e.g. benzyl chloride and benzoyl chloride, undergo reduction or hydrogenolysis, whereas cyano and carbonyl groups (except in quinones and α-diketones) do not react. H. H. H.

N-Fluoroalkylanilines and their N-Hydroxyalkyl Derivatives—Preparation and Properties. J. B. Dickey, E. B. Towne, M. S. Bloom, G. J. Taylor, H. M. Hill, R. A. Corbitt, M. A. McCall, and W. H. Moore. *Ind. Eng. Chem.*, **46**, 2213–2220 (Oct. 1954).

A series of *N*-fluoroalkylanilines were prepared by treating anilines with various fluoroalkyl halides, e.g. *N*-2:2:2-trifluoroethylaniline from—

A number of new fluoroalkyl halides were prepared for this purpose, and other known compounds were prepared by improved methods. Alkylation temperatures varied with the reactivity of the fluoroalkyl halide and the basicity of the substituted aniline. The following fluoroalkyl groups were introduced by alkylation—2-fluoroethyl, 2:2-difluoroethyl, 2:2:2-trifluoroethyl, 2:2-difluoropropyl, 3:3-difluoropropyl, 3:3:3-trifluoropropyl, 3:3-difluorobutyl, and 4:4-difluoropentyl. *N*-(1*H*:1*H*-heptafluorobutyl)-aniline was prepared by reduction with Li amalgam of heptafluorobutyranilide. The *N*-fluoroalkyl-*N*-hydroxyalkylanilines were prepared by alkylation of the *N*-fluoroalkylanilines with ethylene oxide, propylene oxide, 3-bromo-1-propanol, and 3-chloro-1:2-propanediol, e.g. *N*-2:2:2-trifluoroethyl-*N*-2-hydroxyethylaniline from—



The chemical and physical properties of both series of compounds are influenced by the degree and position of fluorine substitution. The compounds are used as coupling components in the preparation of azo dyes for acetate rayon which have good fastness to light and to gas-fume fading. W. K. R.

Absorption Spectra of Some p-Aminoaryldiazonium Derivatives. L. C. Anderson and J. W. Steedly. *J. Amer. Chem. Soc.*, **76**, 5144–5146 (20 Oct. 1954).

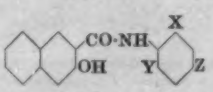
p-Aminoaryldiazonium salts and some of their derivatives are extremely stable compared with most simple diazonium compounds. Their colour, instability to light, and coupling properties make them of great value in photochemical reproduction processes. Comparison of the absorption spectral curves of *p*-amino-, *p*-methylamino-, and *p*-phenylamino-phenylene diazoimine, the corresponding diazonium salts, and *p*-dimethylamino-benzenediazonium chloride with those of diphenylquinomethane indicates that they have a quinonoid structure. C. O. C.

Investigation by means of Infrared Spectroscopy of the Relation between Hydrogen Bonding and Structure in Aminoazo Compounds. G. D. Bagratishvili. *Doklady Akad. Nauk S.S.S.R.*, **96**, 753–756 (1 June 1954).

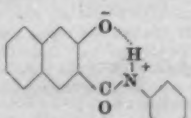
Comparison of the infrared absorption spectra of aniline, 1-naphthylamine, *p*-aminoazobenzene, 4-phenylazo-1-naphthylamine, and 1-phenylazo-2-naphthylamine (as solid, melt, and solutions in various solvents) indicates that the dyes are entirely in the aminoazo form, no quinone hydrazone isomer being present. The spectra of the *p*-aminoazo dyes (three bands in the 3200–3500 cm.$^{-1}$ range) are readily interpreted in terms of vibrations associated with an NH_2 group that can participate in intermolecular hydrogen bonds, but the spectrum of the *o*-aminoazo cpd. is quite different—it has two bands in this range, one of which is weak and diffuse, is essentially unaffected in position by change in state of aggregation, solvent, concn., etc., and is to be attributed to an N–H that is internally bonded to the azo group; the hydrogen so bonded does not readily undergo exchange with deuterium. The other band (intense and sharp, but variable in position) is attributable to the second N–H of the NH_2 group, the hydrogen of which readily undergoes exchange with deuterium. A. E. S.

Structure of Arylamides of Orthocarboxylic Acids relative to their Affinity for Cellulose. M. Delépine. *Compt. rend. Acad. Sci. Paris*, **237**, 69–71 (1953): *Chem. Abs.*, **48**, 11382 (10 Oct. 1954).

Substantivity of the anilide of 2:3-hydroxynaphthalenecarboxylic acid has been attributed to enolisation of the CO·NH group and to conjugation. The derivatives of formula—



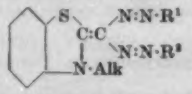
(X, Y, Z = CH_3, CH_3, H; CH_3, O·CH_3, H; O·CH_3, O·CH_3, H; CH_3, CH_3, CH_3; and CH_3, CH_3, O·CH_3) have only slight affinity for cotton, even though enolisation is possible. Probably the affinity of these compounds is caused by the basic solution, in which the HO is ionised. The necessary requirement for substantivity is the possibility of chelate formation, e.g.—



Substitution on the benzene nucleus sterically inhibits the planar configuration which is a prerequisite for chelate formation. C. O. C.

Disazo Dyes. H. Wahl and M. T. Lebris. *Bull. Soc. chim. France*, 587–595 (1954): *Chem. Abs.*, **48**, 11061 (25 Sept. 1954).

Quaternary heterocyclic compounds with a CH_3 group attached in α position to a cyclic N atom couple with 2 mol. of a diazo compound or compounds to give dyes for cotton and cellulose acetate of the type—



(Alk = CH_3 or C_2H_5; R^1 and R^2 = phenyl or subst. phenyl). Thus 1:2-dimethylbenzothiazole methosulphate couples with 2 mol. of diazotised *p*-chloroaniline to give red needles of the disazo dye, soluble in water and pyridine. Similar dyes are made from 2-methylbenzothiazole, 2-methylbenzoselenazole, and quinaldine by coupling with various disazo compounds. E. S.

Chemistry of Dye-forming Development. P. W. Vittum and A. Weissberger. *J. Phot. Science*, **2**, 81–96 (1954): *Chem. Abs.*, **48**, 9847 (10 Sept. 1954).

Practical methods of colour development are restricted to the oxidative condensation of *p*-aminodialkylanilines with couplers. Electro- and stereo-chemical considerations explain the activity of the developers and the reactions of their oxidation products. The various types of open-chain or cyclic active methylene couplers and of methin couplers are surveyed, and coupling sites, elimination coupling, and the stereochemistry of coupling are discussed. Suggested mechanisms of the condensation are discussed and the most likely mechanism is elaborated. Absorption of dyes in solution can be explained by the resonance theory, but additional considerations apply when the dyes are deposited in the image. C. O. C.

Triplet State in Dye Sensitisation. S. Umano. *Hakone Symposium, Japan* (1953); *Science et Inds. phot.*, **25**, 235–236 (1954): *Chem. Abs.*, **48**, 11228 (10 Oct. 1954).

Optical sensitisation by monomeric dye molecules involves energy transfer from the just excited triplet state reached by radiationless transition from the excited singlet state. Data on the temperature coefficient of sensitisation and on the reciprocity failure of optically sensitised emulsion support this theory. C. O. C.

Syntheses of Heterocyclic Compounds of Nitrogen. XC—Photosensitising Dyes—11. T. Takahashi, K. Satake, and S. Yasui. *J. Pharm. Soc. Japan*, **74**, 577–586 (1954): *Chem. Abs.*, **48**, 11412 (10 Oct. 1954).
Syntheses of a large number of methin dyes are described.
C. O. C.

Pyridine Dyes with Negative Substituents in the Aromatic Rings and 1-Aryl Quaternary Salts of Pyridine. N. E. Grigor'eva and I. K. Gintse. *Ukrain. Khim. Zhur.*, **18**, 89–96 (1952): *Chem. Abs.*, **48**, 11411 (10 Oct. 1954).
In presence of pyridine 1-(2:4-dinitrophenyl)pyridinium chloride is cleaved by aromatic amines having negative groups with formation of the corresponding dyes. Decomposition of these dyes yields quaternary 1-arylpyridinium salts. Thus heating the above compound (2·6 g.) with *p*-aminobenzenecarboxylic acid and absolute alcohol (6 ml.) in pyridine (2 ml.) for 1 hr. on a steam-bath yields crystals of a red dye which, washed with ether and alcohol and recrystallised from methyl alcohol, yields lilac needles of

$$p\text{-HOOC-C}_6\text{H}_4\text{-NH-CH:CH-CH: CH-CH:}\overset{+}{\text{N}}\text{H-C}_6\text{H}_4\text{-COOH-}p\}\overset{-}{\text{Cl}}$$

This dye forms a red hemiacetate and on decomposition with alcoholic HCl yields the colourless 1-*p*-carboxyphenylpyridinium chloride.
C. O. C.

Synthesis of Organic Fluorescent Compounds. X—Emissivity of Fluorescence of Naphth[1,2]-iminazoles and Perimidines. Z. Yoshida, Y. Shimada, and R. Oda. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **55**, 354–356 (1952): *Chem. Abs.*, **48**, 11398 (10 Oct. 1954).
Naphth[1,2]iminazole and its 2-CH_3 and 2-C_6H_5 derivatives were synthesised by heating 1:2-$C_{10}H_6(NH_2)_2$.2HCl, the corresponding carboxylic acid, and its Na salt. 1:4-Di(naphth[1,2]iminazol-2-yl)benzene and 1:5-di(naphth-[1,2]iminazol-2-yl)naphthalene were made from 1 mol. of 1:2-$C_{10}H_6(NH_2)_2$ in alcohol and 0·5 mol. of the acid chloride in benzene. The yields were 53·6, 66, 53·4, 40·2, and 61·4% respectively.
C. O. C.

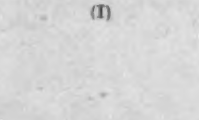
Structure of Overcrowded Aromatic Compounds. I—A Preliminary Survey. E. Harnik, F. H. Herbstein, G. M. J. Schmidt, and F. L. Hirshfeld. *J.C.S.*, 3288–3294 (Oct. 1954).

II—Crystal Structure of Dianthronylidene. E. Harnik and G. M. J. Schmidt. *J.C.S.*, 3295–3302 (Oct. 1954).

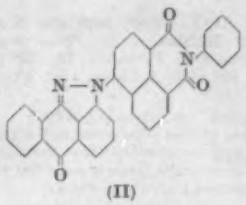
III—Crystal Structure of 3:4-Benzophenanthrene. F. H. Herbstein and G. M. J. Schmidt. *J.C.S.*, 3302–3313 (Oct. 1954).

IV—Crystal Structure of Tetrabenzonaphthalene. F. H. Herbstein and G. M. J. Schmidt. *J.C.S.*, 3314–3319 (Oct. 1954).

Synthesis of Pyrazoloanthrone Vat Dyes. I—Synthesis of 4′-Naphthalimido-*N*-pyrazoloanthrone and its Derivatives. S. Akiyoshi and O. Tsuge. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **56**, 533–534 (1953): *Chem. Abs.*, **48**, 11791 (10 Oct. 1954).
4-Chloro-*N*-phenylnaphthalimide (I) was made by heating anhydrous 4-chloronaphthalic acid (4 g.) with aniline (12) at 180–184°c. for 3 hr. The corresponding *p*-C_2H_5·O·C_6H_4 compound was similarly prepared by replacing the aniline by *p*-phenetidine and heating at 150–160°c. for 5 hr. *N′*-Phenyl-4′-naphthalimido-*N*-pyrazoloanthrone (II) was made by heating pyrazoloanthrone K salt (prepared from pyrazoloanthrone (2 g.) and K_2CO_3 (1·8) in nitrobenzene) with 4-chloro-*N*-phenylnaphthalimide (3 g.) and $CuCO_3$ (0·3) at 210°c. for 7 hr. The corresponding *N′*-ethoxyphenyl derivative was obtained by heating the salt, $CuCO_3$, and *p*-ethoxyphenylnaphthalimide.



(I)



(II)

C. O. C.

Crystal Structure of Indigo. H. von Eller. *Compt. rend. Acad. Sci. Paris*, **238**, 1894–1896 (1954): *Chem. Abs.*, **48**, 11146 (10 Oct. 1954).
Indigo is monoclinic, has one molecule per unit cell, belongs to the space group $P2_1/c$–C^5_{2h}, and has cell dimension $a = 9{\cdot}24 \pm 0{\cdot}03$, $b = 5{\cdot}77 \pm 0{\cdot}02$, $c = 12{\cdot}22 \pm 0{\cdot}03$ A., $\beta = 116°\ 59'$. The zyO, xO_z, and Oyz electron d. projections are given, and also a list of the co-ordinates for the atoms.
C. O. C.

Influence of Ring Size upon the Stability of Metal Chelates. H. Irving, R. J. P. Williams, D. J. Ferrett, and A. E. Williams. *J.C.S.*, 3494–3504 (Oct. 1954).
Although the basic strength of the ligand is greater, the stability constants of the six-membered ring chelates of 1:3-diaminopropane with Cu, Ni, and Cd are lower than those of the corresponding five-membered ring chelate complexes of ethylene- or propylene-diamine. Similar behaviour is characteristic of *β*-alanine and the complexes of malonic and oxalic acid, and corresponding data for a great variety of polydentate ligands support the generalisation that the stability of chelate complexes decreases with increasing ring size. Other factors are also discussed.
H. H. H.

Blue Phthalocyanine Pigments. IV—Thermal Reaction of Phthalic Acid Derivatives with Cuprous Chloride in Ammoniacal Atmosphere. M. Mori. *J. Chem. Soc. Japan, Ind. Chem. Sectn.*, **56**, 595–596 (1953): *Chem. Abs.*, **48**, 11789 (10 Oct. 1954).
Dark blue products were obtained in 18–19% yield by heating phthalic anhydride (30 g.) or phthalimide (30 g.) with anhydrous $CuCl_2$ (6·6–6·9) and H_3BO_3 (1·5) in presence of excess anhydrous NH_3 at 250°c. for 4 hr.
C. O. C.

Crystallisation of Phthalocyanine Blue. R. E. Brouillard and T. D. Mutaffis. *Paint & Varnish Production*, **44**, (7), 30–31 (1954): *Chem. Abs.*, **48**, 11808 (10 Oct. 1954).
Discussion of the factors causing crystallisation and of tests to evaluate the stability of the pigment in enamels. Stable phthalocyanine blues can be made by incorporating a stabilising agent or by grinding the pigment with an extractable grinding aid.
C. O. C.

Photochemical Properties of Metal-containing Analogues of Chlorophyll. M. S. Ashkinazi and V. E. Karpit-skaya. *Doklady Akad. Nauk S.S.S.R.*, **96**, 785–788 (1 June 1954).
Iron, zinc, and copper analogues of chlorophyll are prepared, and it is shown that in each case irradiation with visible radiation in absence of oxygen leads to irreversible reduction via intermediate coloured substances to ultimate colourless products. The iron analogue is readily oxidised to an extremely light-sensitive form, this change being reversible and evidently associated with change in the valency state of the iron.
A. E. S.

Photochemical Reduction of Phaeophytins a and b. V. B. Evstigneev and V. A. Gavrilova. *Doklady Akad. Nauk S.S.S.R.*, **96**, 1201–1204 (21 June 1954).

Reversible Photochemical Reduction of Haematoporphyrin to Chlorine and Bacteriochlorine. A. A. Krasnovskiĭ and K. K. Voĭnovskaya. *Doklady Akad. Nauk S.S.S.R.*, **96**, 1209–1212 (21 June 1954).

The System Al_2O_3–Cr_2O_3 and the Red Colour of Synthetic Rubies. E. Thilo and J. Jander. *Forschungen und Fortschr.*, **26**, 35 (1950): *Chem. Zentr.*, **2**, 649 (1951): *Chem. Abs.*, **48**, 9781 (10 Sept. 1954).

Cr is tervalent in all Al_2O_3–Cr_2O_3 mixed crystals. Synthetic rubies of this type must not contain more than about 8% Cr_2O_3, otherwise they lose their purity of colour, which gradually changes from a pure red to green as the Cr content increases above this value. C. O. C.

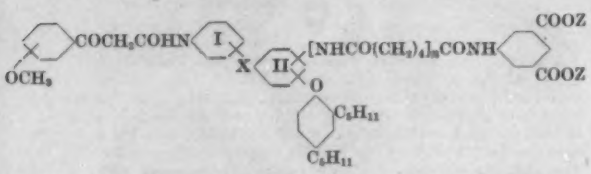
Ultramarine Blue. II— Preparation. P. D. Pant and J. B. Lal. *J. Proc. Oil Technol. Assocn. India, Kanpur*, **7**, 116–119 (1951): *Chem. Abs.*, **48**, 10355 (10 Sept. 1954).

Ultramarine rich in silica was prepared satisfactorily using various recipes. Heating for 20 hr. instead of the usual 10 hr. can result in a better colour. Variations in the amounts of Na_2SO_4 and Na_2CO_3 result in a poor product. C. O. C.

PATENTS

Photographic Colour Couplers. Eastman Kodak Co. *USP* 2,652,329

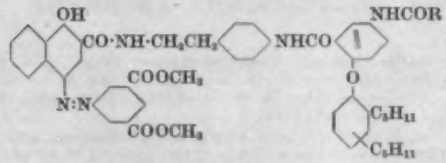
Compounds of formula—



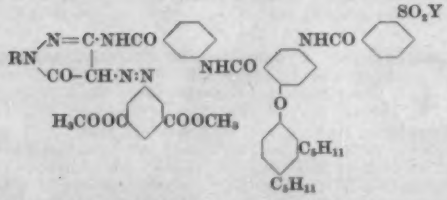
(X = CONH, CH_2CONH, $(CH_2)_2CONH$, $(CH_2)_3CONH$, $(CH_2)_4CONH$, OCH_2CONH, $O(CH_2)_2CONH$ or CH:CHCONH; Z = Alk or an alkali metal; n = 0 or 1; radical I is linked to X in the m or p position; radical II is substituted o or m to X) are photographic colour couplers which can be readily recrystallised. C. O. C.

Colour Couplers containing *iso*Phthalic Ester Groups. Eastman Kodak Co. *USP* 2,657,134

Compounds of formula—



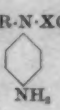
or



R = mononuclear Ar; Y = OH or arylamino) are colour couplers which can be incorporated directly into photographic emulsions. C. O. C.

Dyes for Diazotypes having Increased Fastness to Acid Fumes. General Aniline. *USP* 2,655,448

Introduction of *N*-alkylol groups into conventional light-sensitive diazo dyes yields dyes which are more brilliant and faster to acid fumes than the original dyes but which are less fast to water. This defect can be overcome without loss of the other desirable properties if the alkyl group is esterified. Dyes containing these groups can be produced by using amines of formula—



(R, X and Y = same or different Alk) as the diazo component. C. O. C.

Monoazo Acid Reds. S. *BP* 716,353

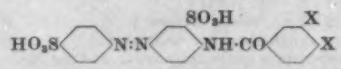
p-Alkylanilines, Alk of 4–5C, are diazotised and coupled with 1-acylamino-8-naphtholdisulphonic acids to give red acid dyes. Thus the monoazo dye *p*-*n*-butylaniline→1-(2′:4′-dichlorobenzoyl)amino-8-naphthol-3:5-disulphonic acid dyes wool, silk and nylon bright blue-reds from a neutral or weakly acid bath. E. S.

Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc. Ciba. *BP* 716,753

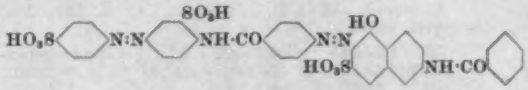
Monoazo dyes *o*-aminophenol→acylacetic ester or amide, containing at least one sulphamyl group, but no SO_3H or COOH groups, are converted into cobalt complexes containing 1 atom Co to 2 mol. of monoazo dye. The products dye wool and nylon from weakly alkaline, neutral, or weakly acid baths. Thus the monoazo compound 2-aminophenol-4-sulphonmethylamide→acetoacet-*o*-chloroanilide dissolved in aq. NaOH is heated at 80–85°C. with aq. $CoSO_4$. The water-soluble complex so produced dyes wool reddish-yellow. E. S.

Dischargeable Direct Cotton Azo Dyes. S. *BP* 717,000

A diazotised *m*(or *p*)-aminobenzoylaminoazo compound



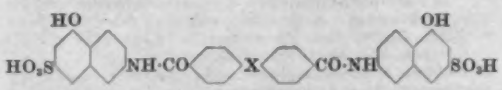
(one X = NH_2, the other X = H, Hal, Alk, or O·Alk) is coupled with an *N*-aryl or *N*-acyl derivative of J acid, γ acid or 5:5′-dihydroxy-2:2′-dinaphthylamine-7:7′-disulphonic acid, or with a suitable pyrazolone derivative to give direct cotton dyes of good brightness and dischargeability. Thus *p*-nitrobenzoyl chloride is condensed with 4-aminoazobenzene-3:4′-disulphonic acid, and the nitro group converted into NH_2. This product is diazotised and coupled at pH 6·5–7 with *N*-benzoyl-J acid to give the bright reddish-orange—



E. S.

Red Polyazo Direct Cotton Dyes for Aftercoppering. Gy. *BP* 717,357

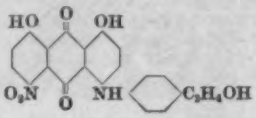
Diazotised 2-aminophenol-4-methylsulphone (2 mol.) is coupled with 1 mol. of—



(X = an azo, azoxy, or urea linkage) made from *N*-*p*-nitrobenzoyl-J acid, either by reducing the NO_2 group to NH_2 followed by treatment with phosgene, or by reducing with glucose, Na_2S, etc. The products are bluish-red direct cotton dyes, suitable for aftercoppering. E. S.

β-Hydroxyalkylphenylamino-Nitro-Hydroxy-Anthraquinones— Disperse Dyes. Eastman Kodak. *BP* 716,333

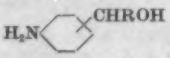
1:8-Dihydroxy-4:5-dinitroanthraquinone is condensed with an aminophenylethyl alcohol to produce blue disperse dyes, fast to light and burnt gas fumes. Thus the dye—



is prepared by heating β-*p*-aminophenylethyl alcohol and 1:8-dihydroxy-4:5-dinitroanthraquinone at 150–155°C. for 4 hr. in quinoline. Separation is effected by pouring into warm aq. HCl.

BP 716,564

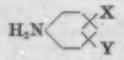
In place of aminophenylethyl alcohol compounds of the type—



where R = H, CH_3 or C_2H_5, are used.

BP 716,937

The condensing amine used is of general formula—

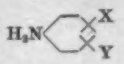


where X = mono-β- or -γ-hydroxyalkyl having 3C; dihydroxyalkyl having 3C; $-(OCH_2CH_2)_nOH$, where n = 1–4; or $-(OCH_2CH_2)_mOR$ where m = 1–3 and R = CH_3 or C_2H_5; and Y = H, CH_3, OH, OCH_3 or Cl.

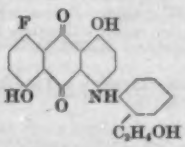
R. K. F.

β-Hydroxyalkylphenylamino-Halogeno-Hydroxy-Anthraquinones—Disperse Dyes. Eastman Kodak. *BP* 716,688

A 1:5-dihalogeno-4:8-dihydroxyanthraquinone is condensed with an amine of general formula—



(where X = monohydroxyalkyl having 1–3C, or dihydroxyalkyl having 2 or 3C; and Y = H, CH_3, OH, OCH_3 or Cl) to give blue disperse dyes, fast to light and gas fumes. Thus the dye—



is prepared by heating 1-chloro-4:8-dihydroxy-5-fluoro-anthraquinone with an excess of *o*-aminophenylethyl alcohol at 160–170°C. for 4 hr., adding ethanol and pouring into aq. HCl.

R. K. F.

Disperse Dyes from 4:8-Dinitroanthrarufin. Celanese Corpn. of America. *BP* 717,011

The affinities for cellulose acetate of the dyes obtained in *BP* 646,459 (J.S.D.C., **67**, 160 (1951)), i.e. the products of condensing 4:8-dinitroanthrarufin and a primary amine, are improved by treating them at 100–130°C. with a > 9% solution of an alkali, e.g. KOH, in a water-miscible liquid, e.g. ethanol.

R. K. F.

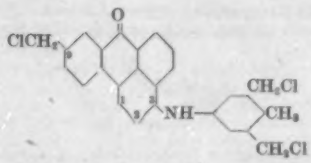
2:3-Dihalogeno-1:2:3:4-tetrahydroanthraquinones. American Cyanamid Co. *USP* 2,642,445

By treating 1:4-dihydroanthraquinone with a halogen, the addition compound carrying halogen atoms at positions 2- and 3- is formed. Thus bromine is added slowly to a suspension of 1:4-dihydroanthraquinone in carbon tetrachloride at 0–5°C.

R. K. F.

Chloromethylated Arylaminobenzanthrones and derived Quaternary Compounds. General Aniline. *USP* 2,642,442

Arylaminobenzanthrones are treated with bis-chloromethyl ether to give derivatives having chloromethyl group(s) in the aryl nucleus and in some cases in the 9-position. Thus 3-(*p*-toluidino)-benzanthrone is heated at 63°C. for 15 hr. in H_2SO_4 with bis-chloromethyl ether to produce—



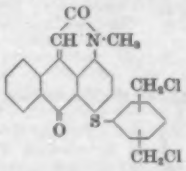
USP 2,642,443

Compounds of the above type are treated with either a tertiary nitrogen base or a thiourea to produce a quaternary compound or an *iso*thiouronium salt respectively. Both are soluble dyes suitable for printing cellulose materials or colouring paper pulp. Thus the chloromethyl derivative having the above formula is heated at 100°C. for 15 min. with aq. 1:1:3-trimethylthiourea, and the product separated by pouring into acetone.

R. K. F.

Chloromethylated Anthraquinone-Arylthioethers. General Aniline. *USP* 2,642,444

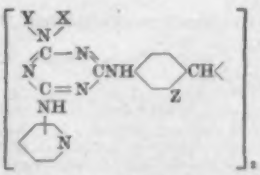
Anthraquinone-aryl thioethers are treated with bis-chloromethyl ether, when $-CH_2Cl$ group(s) enter the aryl nucleus to give derivatives which may further be converted into the corresponding quaternary or *iso*thiouronium salts. Thus 4-phenylthio-anthrapyridone is heated at 60°C. for 16 hr. with bis-chloromethyl ether in H_2SO_4 to produce the compound—



R. K. F.

Fluorescent Brightening Agents. General Aniline. *USP* 2,658,064

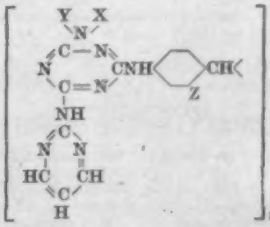
Compounds of formula—



(YXN- = NH_2 or the residue of a primary or secondary amine; Z = COOM or SO_3M (M = H or a cation)) are obtained by condensing a 4:4′-diaminostilbene sulphonic (or carboxylic) acid with cyanuric chloride, this product is then condensed first with an aminopyridine and finally with ammonia or a primary or secondary amine. They are very efficient fluorescent brightening agents substantive to cellulose.

USP 2,658,065

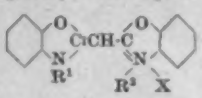
Compounds of formula—



are obtained if the aminopyridine is replaced by 2-amino-pyrimidine.

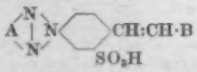
C. O. C.

Fluorescent Brightening Agents. Ilford. *BP* 718,119
Blue-fluorescing oxacyanine compounds of formula—



(R^1 and R^2 = same or different Alk; X = residue of a strong inorganic or organic acid; both benzene rings may contain further substituents) have marked affinity for starch and permanent finishes for textiles, e.g. urea-formaldehyde condensates, polyvinyl acetate emulsions, quaternary salts of formaldehyde long chain fatty acid amide condensates, etc. Used in such finishes they impart fluorescent brightening and do not tend to separate and cause surface blooming. C. O. C.

Monotriazole Fluorescent Brightening Agents. Gy. *BP* 717,889
Compounds of formula—

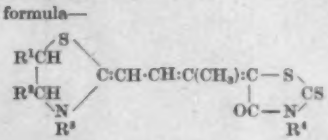


(A = subst. or unsubst. naphthalene in neighbouring $\alpha\beta$-positions to the N atoms; B = subst. or unsubst. benzene) and their salts are weakly yellowish and show blue fluorescence. They have good affinity for cellulose on which they have good fastness to light and very good fastness to chlorine. They can also be used for an acid bath, and in some cases from a neutral bath, for brightening wool and nylon. C. O. C.

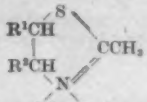
Non-crystallising Phthalocyanines. Kemisk Vaerk Koge. *BP* 716,324
The tendency of phthalocyanines to crystallise and lose tinctorial power, when in contact with, e.g. aromatic hydrocarbons, is reduced by mixing with them ca. 10% magnesium phthalocyanine with or without in addition ca. 10% of an organic amine of dissociation constant $> 4 \times 10^{-7}$, e.g. dodecylamine.

BP 716,325
Additions of the organic amine only are made for the same purpose. R. K. F.

Asymmetric Cyanine Dye. Haloid Co. *USP* 2,653,152
Dyes of formula—

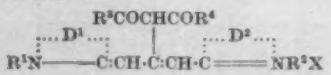


(R^1 and R^2 = H or Alk; R^3 = Alk; R^4 = Alk or Ar) are formed by treating an *N*-subst. rhodanine in an inert organic solvent and in presence of an organic base with a quaternary salt of a 2-methylthiazoline compound, e.g.—



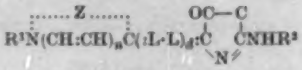
(X = anion) is treated with an *N*-subst. rhodanine in which the substituent on the N atom is Alk or Ar. C. O. C.

Cyanine Dyes. Ilford. *BP* 717,858
Dyes of formula—



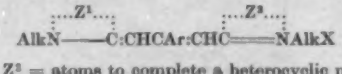
(R^1 and R^2 = Alk; R^3 = Alk or Ar; R^4 = Alk, Ar, alkoxy or amino; $R^3 + R^4$ contain < 12C; X = anion; D^1 = benzothiazole residue; D^2 = residue of benz- or naphtha-thiazole, benzselenazole or benzoxazole) are photographic sensitisers. C. O. C.

***mero*Cyanine Dyes containing a 2-Acylamino-5(4)-thiazolone Group.** Eastman Kodak Co. *USP* 2,652,397
Dyes of formula—



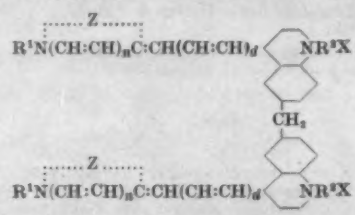
(R^1 = Alk or acyl; L = subst. or unsubst. methin; n = 0 or 1; d = 0, 1 or 2; Z = atoms to complete a 5- or 6-membered nucleus) are useful photographic sensitisers. C. O. C.

***meso*-Substituted Carbocyanine Dyes.** Eastman Kodak Co. *USP* 2,652,330
Dyes of formula—



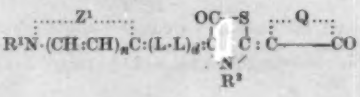
(Z^1 and Z^2 = atoms to complete a heterocyclic nucleus of the benzothiazole series; X = anion) are supersensitisers for photographic use. C. O. C.

Bis-cyanine Dyes. Eastman Kodak Co. *USP* 2,652,396
Dyes of formula—

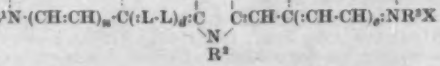


(d and n = 0 or 1; R^1 and R^2 = same or different subst. or unsubst. Alk; X = anion; Z = atoms to complete a thiazole, benzthiazole, naphthothiazole, benzoxazole etc.) are excellent photographic sensitisers. C. O. C.

Trinuclear Dyes containing a 5-Thiazolidone Nucleus. Eastman Kodak Co. *USP* 2,656,351
Dyes of formula—

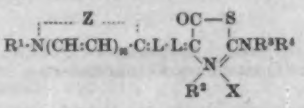


or



(R^1, R^2 and R^3 = same or different, Alk, hydroxyalkyl, or acylalkyl, R^3 may also = *cyclo*alkyl; e and n = 0 or 1; d = 1 or 2; X = anion; L = methin; Z^1 and Z^2 = same or different atoms to complete a 5- or 6-membered ring), are photographic sensitisers. C. O. C.

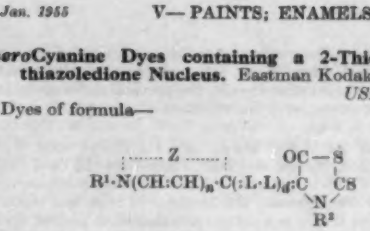
Quaternary Salt Dyes derived from 2-tertiary Amino-5(4)-thiazolones. Eastman Kodak Co. *USP* 2,656,352
Quaternary salt dyes of formula—



(R^1 and R^2 = subst. or unsubst. Alk; R^3 and R^4 = Alk or Ar or together = atoms to complete a 6-membered ring; n = 0 or 1; L = methin; X = anion; Z = atoms to complete a 5- or 6-membered ring) are photographic sensitisers. C. O. C.

***mero*Cyanine Dyes containing a 2-Thio-2:5(3:4)-thiazoledione Nucleus.** Eastman Kodak Co. *USP* 2,656,353

Dyes of formula—



(R^1 = subst. or unsubst. Alk; R^2 = subst. or unsubst. Alk or *cyclo*alkyl; L = subst. or unsubst. methin; n = 0 or 1; d = 1 or 2; Z = atoms to complete a 5- or 6-membered ring) are photographic sensitisers. C. O. C.

Furnace Black. Godfrey L. Cabot. *USP* 2,652,313

An improvement on the General Atlas type process (*USP* 1,904,469) which increases the yield by 50%. C. O. C.

Carbon Black. Columbian Carbon Co. *USP* 2,659,662–3

Reducing the pH of Furnace Blacks. Phillips Petroleum Co. *USP* 2,657,117

Rendering Dyes, Azoic Coupling Components and other Solids Water-dispersible. ICI. *BP* 717,840

Water-insoluble or sparingly soluble solids, e.g. dyes or azoic coupling components, are readily dispersed in water if they are previously mixed with a water-soluble salt of polysulphonated styrene, preferably by adding the polysulphonated styrene to an aqueous paste of the solid and then drying. C. O. C.

Apparatus for Producing Carbon Black by the Explosion Process (I p. 53).

Imino-dicarboxylic Acids— Auxiliary Agents and Dyes forming Metal Complexes (III p. 54).

Azo Couplers and Dyes for Use in Colour Photography (IX p. 65).

Developers for Colour Photography (IX p. 66).

Luminescent Resins from Aryl-substituted Alkyl Halides and Alkenyl Ethers of a Polyhydroxy Organic Compound (XIII p. 70).

Interaction of Dyes with Proteins on Paper with special reference to Paper Electrophoresis (XIV p. 70).

V— PAINTS; ENAMELS; INKS

Coatings of Polyamide and Epoxy Resin Blends. M. M. Renfrew, H. Wittcoff, D. E. Floyd, and D. W. Glaser. *Ind. Eng. Chem.*, **46**, 2226–2232 (Oct. 1954).

Combinations of epoxy resins with polyamines of low mol. wt. (e.g. ethylenediamine) provide coatings with valuable properties, but have practical limitations owing to short pot life of the mixture and physiological activity of the amine. By replacing the volatile amine with polyamide resins of low mol. wt. containing reactive amine groups, a longer working life is obtained together with reduced health hazard and lower cost. The polyamide–epoxy resin coatings are extremely flexible and have very high impact resistance. W. K. R.

High-polymer Theory of the Wrinkle Phenomenon. H. Burrell. *Ind. Eng. Chem.*, **46**, 2233–2237 (Oct. 1954).

The observed facts concerning the wrinkling of drying-oil films are explained by a swollen-gel theory, which postulates that a surface skin formed by rapid polymerisation is swollen by the underlying liquid monomer, until the expansive forces cause a folding of the swollen skin, which appears as a wrinkle. W. K. R.

PATENTS

Light-responsive Fluorescent Media. J. L. Switzer and R. C. Switzer. *USP* 2,653,109

A daylight-fluorescing dye is dispersed in a carrier and applied to the surface to be coloured or printed. A colourless ultraviolet absorbing agent, e.g. 2:3-diphenylquinoxaline, 2:3-diphenyl-6-methylquinoxaline, ethylene glycol disalicylate or 5:7-dibromo-8-hydroxyquinoline, is also either dispersed in the carrier or, preferably, applied as a separate top coating. Coatings or prints obtained by this means are faster to light than those produced in absence of an ultraviolet absorptive agent. The amount of dye must decrease as the daylight fluorescent colour varies from blue to red, e.g. in a blue or green the ratio of dye to carrier may be 10–5% whereas in a red it must not be more than 1%. C. O. C.

Printing Inks for Application to Plasticised Polyvinylbutyral Sheets in Dyeing such Sheets. Monsanto. *BP* 717,387

A suitable ink comprises a polyvinylbutyral resin, an alcohol, ketone, chlorinated hydrocarbon or aromatic hydrocarbon solvent for the resin and a fast-to-light dye soluble in a ketone or chlorinated hydrocarbon. The dye must contain 2–4 cyclic nuclei in the molecule and be capable of diffusing in the resin and at least one of the solvents. The ink must have a viscosity of 10–500 centipoises. Sheets of the resin can be dyed by printing them with the above ink and conditioning the printed sheets at 20–60°C. until they are uniformly coloured. C. O. C.

Aqueous Pigment Pastes. ICI. *BP* 718,374

Aqueous pigment pastes for use in flushing processes are obtained by adding a non-acidic substance which in presence of water yields an acid, e.g. phthalic or maleic anhydride, to a fluid aqueous pigment paste which has been peptised with a soap. C. O. C.

Glossy Enamels and Lacquers containing Polyethylene. DuP. *USP* 2,655,489

The reduction of gloss caused by using polyethylene in enamels and lacquers can be obviated by gelling the polyethylene with a liquid polysiloxane and then grinding it in presence of those components of the enamels which require grinding. C. O. C.

Multicolour Coating Composition. United Lacquer Mfg. Corpn. *USP* 2,658,002

A coating composition containing several colours and which yields a coating in which these colours are related to one another in a predetermined manner has as its base an organic film-forming vehicle together with driers, plasticisers etc. Each of the colouring matters is mixed with a suitable mill base and taken up with a clear film-forming base. Each of these coloured mixtures is then mixed with a protective colloid and finally all are mixed together to form the final composition. The product is stable and yields a coating in which the several colours distribute themselves in a discrete manner. Suitable proportioning of the several colours and control of the ingredients enables predetermined colour patterns to be produced. C. O. C.

Plasticisers for Cellulose Nitrate Coating Compositions (III p. 55).

Crystallisation of Phthalocyanine Blue (IV p. 57).

Colourless Printing Fluid to produce Different Colours on Differently Sensitised Sheets (IX p. 66).

Luminescent Resins from Aryl-substituted Alkyl Halides and Alkenyl Ethers of a Polyhydroxy Organic Compound (XIII p. 70).

VI— FIBRES; YARNS; FABRICS

Fibres. J. L. Vodonik, R. S. Casey, and C. S. Grove. *Ind. Eng. Chem.*, **46**, 2076–2083 (Oct. 1954).

Developments in 1953 are reviewed under the headings— synthetic fibres research, cotton fibres research, markets and prospects, industrial uses, non-woven fabrics, coated fabrics, synthetic fibres manufacture, finishes, identification of fibres. There are 77 references. W. K. R.

Mechanical Properties of Cellulose Fibres. W. E. Roseveare and L. Poore. *J. Polymer Sci.*, **14**, 341–354 (Oct. 1954).

Measurements are reported for reversible changes in force with temperature at constant length of wet and dry viscose rayon and wet ramie. Entropies of stretching are interpreted in terms of mechanisms of reversible stretching. Completely dry rayon is glass-like and shows no slippage of chains. Wet rayons show a rubber-like slippage of chains above 50°C.; below this temperature chain movement is restricted. Wet ramie appears to be in the glassy state like completely dry rayon. W. R. M.

Small-angle Scattering of Cellulose Fibres. P. H. Hermans and A. Weidinger. *J. Polymer Sci.*, **14**, 405–407 (Oct. 1954).

The small-angle scattering of some hydrolysed rayon fibres is examined. An intensity maximum is observed on mild acid hydrolysis, suggesting that the regularity of the supermolecular structure is increased. Disappearance of this maximum on drying is attributed to the formation of larger aggregates of irregular size and shape. W. R. M.

X-Ray Scattering of Swollen Rayons. P. H. Hermans and A. Weidinger. *J. Polymer Sci.*, **14**, 397–401 (Oct. 1954).

The small-angle scattering of X-rays by a number of rayons swollen in aqueous LiOH solutions has been studied. With samples showing an intensity maximum in the water-swollen condition, the locus of the maximum shifts to smaller angles on further swelling in LiOH soln. Interparticle interferences make the accurate estimation of particle size unlikely. W. R. M.

Preparation of Viscose by Xanthation of Soda-cellulose Slurry. W. Matthaes. *Faserforsch. und Textiltech.*, **5**, 285–290 (July 1954).

On the basis of laboratory experiments the conditions are determined for the technical xanthation of a dilute soda-cellulose slurry to give fibre-free viscose. Use of the process leads to great savings in time and power, and there are other technical advantages, some of which result from the flow properties of the reaction mixture. A. E. S.

Fine Structure of Viscose and Cuprammonium Rayons. R. Haller. *Melliand Textilber.*, **35**, 965–967 (Sept. 1954).

The structural element of the plant cell wall— the dermatosome of Wiesner— can be shown to persist through xanthation and viscose spinning, but not through the cuprammonium process. If viscose rayon is disintegrated with saturated chlorine water and then swollen with H_2SO_4, a grain structure is apparent. Cuprammonium rayon so treated is structureless and transparent. S. R. C.

Heterogeneous Swelling in the Formation of Wool Properties. M. Zilahi and O. K. Dobozy. *Acta Technica, Acad. Sci. Hungaricae*, **9**, (1–2), 65–120 (1954).

Knowledge of three quantities— the inflexion radius, the wavelength, and the wave line length— is necessary for the exact definition of wool crimp. Mathematical relationships are obtained between fibre diameter and inflexion radius, reciprocal of wavelength, and ratio of length of wave line to wavelength. It is suggested that bending forces causing crimp arise in only part of the fibre, and that these forces are a result of swelling or shrinkage of the fibre. The effects of relative humidity and water uptake on change of crimp are discussed. A state of swelling occurs where less oriented protein is swelled to such an extent that it produces new bending forces, forming new inflexions. Such a state is generally reached in water or aqueous solutions, and results in spontaneous entanglement of fibres, which is suggested as the primary condition of felting. W. R. M.

Action on Wool Fibres of Strong Solutions of Urea containing Reducing Agents. E. H. Mercer. *Text. Research J.*, **24**, 835–841 (Sept. 1954).

It is shown that saturated aqueous solutions of urea containing reducing agents dissolve about 25% of wool fibre at pH 8. The extracted protein is removed from the less stabilised fraction of the cortex, and the residue consists of the cuticular sheath, the cortical cell membranes of the orthocortex, and the resistant paracortex. A. B.

Manganese in Wool Wax. E. V. Truter and F. P. Woodford. *Chem. and Ind.*, 1323–1324 (23 Oct. 1954).

A fraction rich in manganese is isolated from commercial centrifuged wool grease; the absence of iron and silicates suggests that it has not come from fine dust picked up by the raw wool. J. W. B.

Man-made Fibres— Their Diversity and Properties. P. A. Koch. *Teintex*, **19**, 727–769 (Oct. 1954).

A wide and detailed review in which are discussed— economics, historical development and inventors, nomenclature, appearances of cross-sections, solubilities in solvents, thermal properties, water absorption, densities, extensibilities and elasticities, and spheres of application. Much of the information is presented in useful tabular form. S. R. C.

Utilisation of Polyamide Wastes by the Depolymerisation–Filtration Method. H. Ludewig and K. Froeber. *Faserforsch. und Textiltech.*, **5**, 277–284 (July 1954).

On the basis of laboratory experiments on the depolymerisation of polyamides (mainly 6-nylon), a technically simple and satisfactory large-scale method is developed for the utilisation of polyamide wastes. It consists in depolymerisation of the wastes by means of water under pressure, filtration and evaporation of the resulting solution, and repolymerisation of the product. A. E. S.

Macromolecular Compounds. LXIII and LXVI— Heteropolymerisation of Diisocyanates and Glycols. V. V. Korshak and I. A. Gribova. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 550–561 (May–June), 670–676 (July–Aug. 1954).

LXIII— A study is made of the formation of polyurethans from methylenedi-*p*-phenylene diisocyanate and butane-1:4-diol in a nitrobenzene medium (in which the polymers are sol.). Polymers of max. mol.wt. (27,000) are obtained at 145–155°C.; above and below this temp. the mol.wt. falls off rapidly. The mol.wt. of the product increases rapidly with the concn. of reactants, and is greatly reduced when one or other reactant is in excess. Polymer obtained from a mixture containing excess of *iso*cyanate has a higher mol.wt. when solvent is removed by steam distillation rather than by solvent extraction, and this is considered to be due to hydrolysis of *iso*cyanate end-groups to amino groups, which react with unchanged *iso*cyanate end-groups to form urea linkages. Among other topics discussed are the reduction in the mol.wt. of the polymer by addition of monofunctional substances (e.g. octyl alcohol, piperidine) to the reaction mixture and alcoholysis, aminolysis, acidolysis, and *iso*cyanolysis degradation reactions of the polymer.

LXVI— The kinetics of the above heteropolymerisation reaction are studied in detail. In the last stage of the reaction, increase in mol.wt. occurs mainly as a result of reactions between two polyurethan macromolecules. A. E. S.

Effect of Adsorption on Recoverable and Non-recoverable Creep in Stressed Glass Fibres. M. S. Aslanova and P. A. Rebinder. *Doklady Akad. Nauk S.S.S.R.*, **96**, 299–302 (11 May 1954).

Aslanova has already shown (*see* J.S.D.C., **70**, 589 (Dec. 1954)) that glass fibres held under tension in water or solutions of surface-active agents may suffer a loss of up to 50–60% in tensile strength. Further experiments are carried out on glass fibres of the same types immersed in the same liquids (*loc. cit.*), and changes in length due to prolonged application of a tension equal to 60% of the ultimate breaking load are observed. In water and solutions of anionic surface-active agents, recoverable creep occurs; thus, in water the creep attains 7% (of the initial extension), completely recoverable when tension is removed, and it is increased to ~ 10% when anion-active solutes are added. Creep is negligible in kerosene (nil for aluminoborosilicate

glass and < 2% for soda glass). For solutions of Velan, and of *iso*pentyl alcohol in the case of aluminoborosilicate glass, the creep is found to have a non-recoverable component (permanent deformation after removal of tension). Creep effects are at their greatest in thick fibres. The results are interpreted on the basis of the surface-defect theory (*loc. cit.*). In accord with deductions from this theory, the etching of glass fibres with hydrofluoric acid greatly increases their tensile strength and renders them less subject to creep. A. E. S.

PATENTS

Treatment of Thread on Continuous Spinning Machinery. Courtaulds. *BP* 716,582

The processing time for the production of viscose rayon is reduced by introducing steam into the interior of the thread-advancing device and emitting at least a portion of the steam into contact with the advancing thread. W. G. C.

Animalised Regenerated Cellulose. American Cyanamid Co. *USP* 2,654,715

Addition of an aminotriazine resin colloid to the spinning solution yields fibres which have good affinity for acid dyes. C. O. C.

Wet-Spinning Polyvinyl Alcohol Fibres. Kurashiki Rayon Kabushiki Kaishi. *BP* 716,951

The stability of spinning solutions of polyvinyl alcohol is improved by adding gelatin, glue, soaps, or turkey red oil. W. G. C.

Improving the Resistance of Polyvinyl Alcohol Fibres to Water and Heat. Kurashiki Rayon Kabushiki Kaishi. *BP* 718,090

The fibres are subjected to a high frequency electric field while they are heated in hot air or superheated steam. The resultant fibres have such increase of their softening point in water as to make them suitable for textile use. If they are subsequently treated with an aldehyde so as to acetylate their hydroxyl groups they are pure white and are stable in boiling water. C. O. C.

Stabilising Synthetic Linear Polymers to Heat. British Nylon Spinners. *BP* 717,698

Incorporation of a small amount (insufficient to cause observable swelling) of a mono- or polyhydric phenol of the benzene or naphthalene series and which may be substituted by Hal, Alk, alkoxy, carboxy or sulpho groups, or an ester or salt of such a phenol increases the stability of polyamides, polyesters, etc. to heat. C. O. C.

Reducing Photochemical Damage to Superpolyamides and Polyurethans. Inventa AG für Forschung und Patentverwertung. *BP* 718,405

Addition of a chromium-containing compound to the monomers, e.g. CrF_3, does not interfere with polymerisation and results in products of better stability to light. C. O. C.

Acrylonitrile Polymers and Fibres. Eastman Kodak Co. *USP* 2,652,378

Difficultly soluble acrylonitrile polymers (≮ 70% by wt. of acrylonitrile units) (70–92 parts by wt.) when mixed with a fumaric amide or an *N*-subst. fumaric amide copolymer with vinyl acetate (30–8) are soluble in common polyacrylonitrile solvents to stable homogeneous solutions. Fibres formed from such solutions dye readily with acid dyes and show increased affinity for disperse dyes and for some types of vat dyes. C. O. C.

Fibres from Vinyl Chloride–Acrylonitrile Copolymers. Chemstrand Corpn. *BP* 717,893

Copolymers of vinyl chloride (35–70%) and acrylonitrile (65–30%) have their thermal and solvent resistances increased by blending them with 2–35% of a polymer containing ≮ 85% of acrylonitrile. C. O. C.

Dyeable Acrylonitrile Copolymers. Chemstrand Corpn. *USP* 2,656,325–6

Triethylamine or trimethylamine is added to a solution of a non-dyeable acrylonitrile–vinyl or methylalkyl halogenoacetate copolymer to impart dyeing properties to it. The amount of the amine should be such as to quaternise a substantial proportion of the halogenoacetate radicals within a reasonable time. Excess amine is then eliminated by adding a compound which converts it into a quaternary ammonium salt. This obviates gelation and increase in viscosity of the solution. The solution can be used to produce high tenacity, dyeable acrylonitrile fibres. C. O. C.

Acrylonitrile Polymers or Copolymers having Affinity for Acid Dyes. Chemstrand Corpn. *USP* 2,656,336

Copolymers of acrylonitrile and a vinyl ester of a halogen substituted monocarboxylic acid are given affinity for acid dyes by treatment with an amine. C. O. C.

Polymerisable Acrylonitrile Compounds which Dye readily. American Cyanamid Co. *BP* 716,340

Acrylonitrile copolymers which are more readily dyed, especially with acid dyes, than homopolymeric acrylonitrile comprise (1) acrylonitrile (99–85% by wt.) and (2) one or more quaternary ammonium compounds of formula

$$[Z—R]^+X^-$$

(Z = tertiary amino group; R = an ethylenic unsaturated hydrocarbon radical of 3–10C terminated by $CH_2=\overset{|}{C}-\overset{||}{C}-$; X^- = anion), e.g. allyltriethylammonium bromide. J. W. B.

Fibre-forming Compositions. Chemstrand Corpn. *BP* 716,472

A fibre-forming polymer comprises 65–98% of a copolymer of a vinyl chloride (30–70% by wt.) and acrylonitrile, and is characterised by being blended with 2–35% by wt. of a polymer of a vinyl-substituted polynuclear ring compound. Such a fibre, formed from 59·8% vinyl chloride : 40·2% acrylonitrile copolymer (90 parts by wt.) and polyvinylcarbazole (10) has a zero strength temperature of 195°C.; the corresponding fibre from the copolymer only, the polyvinylcarbazole being omitted, has a zero strength temperature of 163°C. J. W. B.

Copolymers of 1-Butene Derivatives for producing Fibres having Affinity for Acid Dyes. Chemstrand Corpn. *USP* 2,656,338

Copolymers of compounds of formula—

$$CH_2{:}CH{\cdot}CHOR^1{\cdot}CH_2NR^2R^3X_n$$

(R^1 = H or acyl of 1–12C; R^2 = Alk or Ar, when Alk the two radicals may be joined through C, O or N to form a cyclic radical attached to the N of the butene-1 derivative; X = anion; *n* = 0 or 1) with at least one other different $CH_2{:}C<$ containing compound are fibre-forming and can be dyed with acid dyes. C. O. C.

Polyheptamethyleneurea Fibres. American Viscose Corpn. *USP* 2,653,144

Polyheptamethyleneurea remains unchanged in viscosity and can be drawn into filaments of uniform denier for at least one hour after being heated to 250–280°C. if aniline, unsymmetrical diphenylurea, diphenylamine, hexamethylenediammonium acetate or acetic acid is present as a viscosity stabiliser. Preferably the stabiliser is present when the polyheptamethyleneurea is formed by heating equimolecular proportions of heptamethylenediamine and urea or heptamethylene di*iso*cyanate. C. O. C.

High-tenacity Filaments of Polythiourea. Courtaulds. *BP* 717,968

High tenacity filaments are obtained by extruding polythiourea, treating with an epoxy compound to impart increased stability to heat and before, during, or after the epoxy treatment stretching the filaments at least 50% while they are at ≮ 45°C. Further heat treatment may then be given to prevent shrinkage, this treatment being preferably carried out in hot aqueous medium in absence of tension. C. O. C.

Solvents for Polyacrylonitrile (III p. 55).
Determination of Microcrystallite Size in Rayons (XIV p. 71).
Assessment of Chemical Damage to Cellulosic Textiles during Industrial Bleaching (XIV p. 71).
Application of Radiochemical Techniques to the Study of the Interaction of Hair Fibres with Aqueous Solutions (XIV p. 71).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Soiling of Textile Materials. W. H. Rees. *J. Textile Inst.*, **45**, P612–P631 (Oct. 1954).

A survey of the nature of atmospheric particles and factors leading to their deposition on textiles and other substances and of the nature of soil— greasy, solid, and stains— is followed by a brief account of the assessment of soiling by measurement of reflectance. Experiments are described in which various soiling techniques, including a dust circulator, clouds, and thermal precipitation, are used, and examples are presented of results together with photographs of soiled cotton fabrics. Other fabrics are exposed to the laboratory atmosphere while electrical potentials are applied, the resulting precipitation being assessed by means of electron micrographs. It is shown independently that visible soiling is greatest with positively charged, less with negatively charged, and least with uncharged yarns; this result agrees with values obtained on charged fabrics. At any given potential the extent of visual soiling increases with increasing openness between the yarns. It is also suggested that earthed components of a machine, e.g. in warp knitting, might contribute to soiling by accumulating dirt particles repelled by the charged warp yarns. Methods for estimating dry contact and wet contact soiling, including the degree of adhesion, are also given. Thermal precipitation and oil-free carbon particles deposited by the wet-cloud technique give high adhesion; fog-marked cellulose acetate and nylon have the highest adhesion of all, this being in line with mill experience, where such faults are very resistant to normal scouring. J. W. B.

Effect of Electrolytes on Soil Redeposition in Laboratory and Laundry Practice. P. T. Vitale. *J. Amer. Oil Chem. Soc.*, **31**, 341–344 (Aug. 1954).

Fatty-acid soaps and pure synthetic detergents have a far greater suspending power for Aquadag (Acheson) soil (22% solids paste of colloidal graphite in water with a small amount of suspending agent) than either of these types when used in the presence of inorganic salts. Any inorganic salts of the type of NaCl, Na_2SO_4, Ca or Mg salts, common alkali or phosphate builders, all tend to cause deposition when used alone or with surface-active materials. Fatty-acid soaps are self-protecting against hard-water salt effects.

Synthetic detergents require protection against Ca and Mg salts, which can be achieved by adding calcium-ion suppressants. When neutral salts are present in minor amounts, the use of protective colloids, such as carboxymethyl cellulose, affords some protection. P. G. M.

PATENTS

Wool Scouring. U.S. Secretary of Agriculture. *USP* 2,655,428

A scouring liquor is used containing a neutral, polar, oxygenated organic compound, e.g. a 2% aqueous soln. of *n*-butanol, and preferably in addition a neutral electrolyte. During scouring the suint dissolves in the liquor and its effectiveness in emulsifying the wool grease is enhanced by the presence of the above compound or compounds. The scoured wool is clear and lofty and low in residual grease and residual ash. C. O. C.

Compressional Wave Energy in the Upper Sonic and Supersonic Range for Washing Textiles. Lever Brothers Co. *USP* 2,650,872

Complete washing is obtained with use of a relatively low power, i.e. low intensity, compressional wave energy source by causing standing waves set up in the liquid to be moved systematically relatively to the goods being washed. C. O. C.

VIII— DYEING

Basic Mechanisms of Dye Absorption during Pad-dyeing. H. B. Mann. J.S.D.C., **71**, 7–12 (Jan. 1955).

A study of the basic mechanisms of dye absorption during pad-dyeing has shown that direct dyes are taken up by viscose rayon filament and staple fabrics in two ways— (*a*) adsorbed at the surface of the individual filaments, and (*b*) in dye solution mechanically held within the fabric structure. Differential absorption of dye and water has been clearly demonstrated. This must always be present in principle, although it may become overshadowed by substantive dyeing of the fibre at high padding temperatures or after prolonged immersion in the dyebath. AUTHOR

Affinity Effects during Padding. W. J. Marshall. J.S.D.C., **71**, 13–20 (Jan. 1955).

The advantages and disadvantages of continuous dyeing methods are briefly discussed. A factor of great importance in these processes is the change in colour during the initial period of the run, which makes shade matching and running to shade a matter of considerable skill. This is due to the change in concentration of the pad liquor caused by the affinity of the dye and similar effects. Assuming the simplest possible relations, the magnitude of this change has been calculated, and measurements of a practical system have shown that this mathematical treatment is adequate to characterise the system. Finally, the practical significance of this work is discussed. AUTHOR

Continuous Ribbon Dyeing. L. J. Clarke. J.S.D.C., **71**, 26–28 (Jan. 1955).

A method for the continuous dyeing of ribbon is described in which uniformity of shade over long runs is attained by introducing feed liquor into the dyebath through fine jets, thus maintaining turbulent conditions and uniformity of composition throughout the bath. AUTHOR

Union Dyeing of Blends of Wool and Synthetic Fibres with Water-soluble and Disperse Dyes. AATCC New York Section. *Amer. Dyestuff Rep.*, **43**, P656–P672 (27 Sept. 1954).

Means of overcoming the problems raised by the poor fastness of disperse-dye staining in the dyeing of wool–synthetic fibre blends are studied, with specific reference to wool–acetate rayon, wool–dynel, and wool–Dacron. After a survey of the literature, experiments are described under the following headings— wool staining as a function of dye type and dyebath concn., effect of dyebath acidity on aggregation of disperse dyes, effect of dispersing agents on wool staining, and effect of residual oil content on degree of wool staining. Among noteworthy points, many of which confirm earlier work, are the facts that some disperse dyes are adversely affected by acid in the dyebath, and therefore must be avoided, that non-ionic dispersing agents are best, that wool staining is related to the amount of disperse dye in solution, and that residual oil should preferably be removed prior to dyeing. In the light of these findings, three general instructions are given for the dyeing of blends, followed by five detailed recipes for different blends and types of material, and appendixes covering 7 pp. of tabulated data summarising the properties of the dyes tested. J. W. B.

Factors affecting the Absorption of Disperse Dyes by Dacron Polyester Fibre from Aqueous Baths. J. J. Iannarone, O. S. Larson, and R. J. Thomas. *Amer. Dyestuff Rep.*, **43**, P650–P655 (27 Sept. 1954).

Factors affecting the absorption of disperse dyes by Dacron are studied (1) at 205–208°F. with *o*-phenylphenol (I) as carrier and (2) at 250°F. with no carrier. The influences of temperature and time of dyeing, nature and concentration of carrier, and liquor ratio on the absorption are also discussed. It is found that most disperse dyes have good stability at 250°F., and transfer better than at 205–208°F. with either (I) or benzoic acid as carrier. Data are presented to demonstrate that absorption decreases as the volume increases with both methods, provided that the ratio of carrier (where used) to fabric is constant. If the amount of carrier is based on the liquor, the absorption increases with volume. At 250°F. dyes applied in combination show distribution values between bath and fibre similar to those obtained singly, irrespective of their rates of absorption. Time of dyeing, as related to absorption, is less significant with optimum carrier concentration than with a minimum quantity. Concn. of (I) of 3–6 g./litre at 60 : 1 liquor : fibre ratio and 6–9 g./litre at 20 : 1 ratio give optimum absorption. No serious adverse effects on the physical properties of the fibre are caused by the carrier. J. W. B.

PATENTS

Dyeing with Vat and Sulphur Dyes in a Standfast Molten Metal Machine. Standfast Dyers & Printers. *BP* 717,059

The goods are impregnated under heavy squeezing action with a dye liquor containing a reduced vat or sulphur dye, and are then passed through an aqueous treating liquor floating on the molten metal bath into the molten metal. The treating liquor may be either a solution of solubilising chemicals or dye liquor similar to that used for the impregnation, or simply water. This liquor prevents air being carried into the molten metal by the fabric and also prevents the fabric being penetrated by the molten metal. C. O. C.

Preventing Rise of pH during Dyeing. Br. *BP* 716,990

When dyeing wool, nylon, etc., the pH of the bath may be kept constant or be reduced as desired by having in the dyebath an organic ester having a high and steady rate of hydrolysis and which is present in such amount that the acid formed by the hydrolysis is at least sufficient to prevent $> 0{\cdot}2$ rise in pH during dyeing. Suitable esters include ethyl lactate and diethyl tartrate. C. O. C.

Dyeing Protein or Superpolyamide Fibres with Acid Dyes by the Molten-metal Process. ICI. *BP* 716,575

Wool, Ardil and nylon may be successfully dyed with acid dyes by the process described in *BP* 620,584 (J.S.D.C., 65, 412 (1949)), if the dye liquor floating on the molten metal is either neutral or weakly alkaline and contains a non-ionic surface-active agent. C. O. C.

Dyeing Copolymers of Acrylonitrile and Vinylpyridine. Courtaulds. *BP* 718,734

The affinity of copolymers of acrylonitrile and vinylpyridine, with or without other monomeric compounds, for dyes normally applied from acid, neutral or weakly alkaline baths is improved by treatment with a dilute aqueous solution of an acid of dissociation constant $> 1 \times 10^{-5}$, e.g. with 1% aq. H_2SO_4 at the boil for 10 min. C. O. C.

Dyeing Acetate Rayon with Vat or Sulphur Dyes. Standfast Dyers & Printers. *BP* 716,954

When applying vat or sulphur dyes to acetate rayon in a Standfast molten metal machine very good results are obtained if the dye liquor contains the dye, caustic alkali, a reducing agent and any desired dyeing auxiliaries and is maintained at 80–100°C. The best results are obtained if the acetate rayon is heated to 85–95°C. before entering the dye liquor. C. O. C.

Level Dyeing or Printing of Nylon. Maifoss. *BP* 716,637

Addition to the dyebath or printing paste of $< 0{\cdot}75\%$ on the wt. of goods or $< 0{\cdot}0025\%$ by wt. on the wt. of liquor, whichever is the less, of a water-soluble condensate of urea or formaldehyde with a sulphonic acid of an aromatic compound containing one or more phenolic hydroxyl groups, e.g. Erional NW (Gy), gives improved levelling with all classes of dyes having affinity for nylon. Use of this method enables the heels of footwear to be "struck" even when using the more difficult levelling dyes. C. O. C.

Dyeing Polyacrylonitrile Fibres with Acid and Direct Dyes. DuP. *USP* 2,653,074

Deep level dyeings are produced with acid and direct dyes by use of aqueous baths at pH 1·5–5 in presence of Cu salts (0·25–3·0% on wt. of fibre of cuprous ion) and hydroxylamine (0·15–3·2%) at 190–250°F. C. O. C.

Dyeing Polyacrylonitrile with Disperse Dyes. DuP. *USP* 2,654,652

Deep dyeings fast to light and washing are obtained by padding with a concentrated solution of a disperse dye in a lactone or cyclic carbonate ester of 3–5C, e.g. propiolactone or ethylene cyclic carbonate, and treating the wet padded material with saturated steam. C. O. C.

Principles governing the Efficiency of a Padding Mangle (I p. 53).
Printing Inks for Application to Plasticised Polyvinylbutyral Sheets in Dyeing such Sheets (V p. 61).
Application of Radiochemical Techniques to the Study of the Interaction of Hair Fibres with Aqueous Solutions (XIV p. 71).

IX— PRINTING

Rise and Decline of the Swiss Calico Printing Industry. R. Traupel. *Ciba Rev.*, 9, 3766–3774 (Aug. 1954). **The "Indiennes" Manufacture of Neuchâtel** *Ibid.*, 3777–3781. **The Cloth Printing Trade of Glarus.** *Ibid.*, 3785–3791.

Historical. C. O. C.

Swiss Textile Printing Today. A. Bolliger. *Ciba Rev.*, 9, 3762–3764 (Aug. 1954).

A brief account of the modern textile-printing industry in Switzerland, including a comparison with what it used to be. C. O. C.

PATENTS

Pigment Pastes. Imperial Paper & Color Corpn. *USP* 2,656,327

Aqueous pigmented pastes, prepared by combining in absence of emulsions or organic solvents a cationic, water-soluble thermosetting resin with anionic dispersions of pigment and resin, yield prints which have excellent fastness to washing, light and rubbing. C. O. C.

Use of Indicators in Alkaline Printing Pastes to show up Faults before Development or Fixation. Fran. *BP* 717,252

When using alkaline printing pastes faults in printing are easily detected if there is added to the paste, *o*-cresolphthalein, thymolphthalein, α-naphtholphthalein, tetrachlorophenolphthalein or *o*-cresolsulphonephthalein. If desired an acid dye may also be added. C. O. C.

Photomechanical Resist Compositions. Kodak. *BP* 717,708–12

Describes use of cinnamic acid esters of polymeric materials, especially polyvinyl alcohol and cellulose, in the preparation of printing plates by photosensitising the esterified polymers, and exposing and washing away the unexposed layer with a solvent for the ester. Use of many compounds, including various triphenylmethane dyes, as sensitisers is mentioned. C. O. C.

Colour Photography. Gevaert Photo-Producten and Chromart Film Industries. *USP* 2,659,671

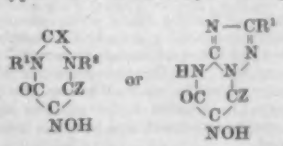
A method of obtaining the impression of trichromatic images from bi-colour negatives. C. O. C.

Colour Photography. Tru Colour Film. *BP* 718,716

A positive silver image is bleached and then treated with an aqueous solution at pH <7 containing thioamide or selenoamide and an acid dye so as to produce a complex from which the colour image is transferred to a permanent base. The dye solution also contains a substance which reduces the water solubility of the silver halide present in the bleached image. C. O. C.

Azo Couplers and Dyes for Use in Colour Photography. General Aniline. *USP* 2,652,328

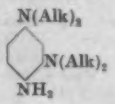
Multilayer colour photographic material to be processed by the silver dye bleachout method contains in the emulsion layers of the taking material colourless non-diffusing azo dye couplers which react with one and the same diazonium salt to yield yellow and magenta dyes, and also a colourless heterocyclic *N*-compound which can be bleached out and which with a metal salt forms a cyan metal complex. The printing material contains yellow and magenta non-diffusing azo dyes which can be bleached out and a colourless *N*-heterocyclic compound of the above type. The *N*-heterocyclic compound is of formula—



(X = O, S, NY or NY_2; Y = H, Alk, carboxyalkyl, sulphoalkyl, Ar, alkoxyaryl, arylsulphonyl, sulphoaryl or cyano; R^1 and R^2 = H, Alk or Ar; Z = O or NH).
C. O. C.

Developers for Colour Photography. Eastman Kodak Co. *USP* 2,652,331

Compounds of formula—



(Alk are same or different) surpass most *p*-phenylenediamines in developer activity and couple well with known couplers to yield dye images having no undesirable variations in light absorption characteristics.
C. O. C.

Stabilised Azine Photographic Developers containing Sodium Metaborate as the Sole Alkali. General Aniline. *USP* 2,656,272

Colour developers of the 2:4-diaminoaniline type containing 30–50 g./l. of sodium metaborate as the sole alkali and stabiliser are 2–3 times as stable when Na_2CO_3 is used as the alkali.
C. O. C.

Heat Development of Diazotypes. Radio Corpn. of America. *USP* 2,653,091

Paper is impregnated with a diazonium salt, e.g. *p*-diazodiethylaniline fluoborate, and an azo dye coupler, e.g. phloroglucinol, and then with a heat sensitive acid and its salt, e.g. trichloroacetic acid, as stabiliser. It is then exposed in the usual manner and developed by heating to just below the scorching point of the paper when the acid is decomposed.
C. O. C.

Electrolytic Marking Method. Radio Corpn. of America. *USP* 2,653,126

A carrier support is impregnated with a mixture, e.g. a nitrite and a sulphamate, which generates gas within the carrier if the pH is changed. These bubbles visibly change the opacity of the carrier, e.g. of regenerated cellulose film.
C. O. C.

Recording Paper to be marked by Electrical Means. Standard Telephones & Cables. *BP* 718,115

Modification of *BP* 711,607. Paper is coated on one or both sides with lead thiosulphate or lead sodium thiosulphate in an adhesive vehicle. The paper is placed so that stationary electrodes are on one side and a movable electrode on the other, means being provided to pass a spark between the movable electrode and a stationary electrode.
C. O. C.

Colourless Printing Fluid to produce Different Colours on Differently Sensitised Sheets. National Cash Register Co. *USP* 2,654,673

A colourless fluid, e.g. an oily chlorinated diphenyl containing in solution xanthen-9, *o*-benzoic acid, 3:6-bis-diethylamino-9-*p*-nitroanilin lactam and 3:3-bis(*p*-dimethylaminophenyl)phthalide or 3:3-bis(*p*-diethylaminophenyl)phthalide, is used to make marks of one colour on a record sheet sensitised with e.g. attapulgite, and marks of another colour on a sheet sensitised with e.g. Ca silicate.
C. O. C.

Manifolding Transfer. Standard Register Co. *USP* 2,653,110

The underside of a sheet has a solid colourless or light coloured coating containing a metallic compound and a water-soluble sulphide with which it would form a dark coloured precipitate but for the presence of an acidic manganese salt. This is used as a transfer paper after which the copy is treated with gaseous ammonia to neutralise the manganese salt and so allow metal sulphide to be developed.
C. O. C.

Developing Electrostatic Images. Haloid Co. *USP* 2,659,670

A toner composition for developing electrophotographic prints from an electrostatic image consists of a mixture of synthetic and natural resins and a pigment. The finely divided developer is deposited on the surface bearing the latent image in configuration conforming with the image and is transferred to paper on to which it is finally fused.
C. O. C.

Removing Colour Developer Stain in Azine Dye Images. General Aniline. *USP* 2,657,139

An azine multilayer colour film is colour developed and then rinsed in an aqueous bath containing 0·1–10·0% of HCHO and 0·1–10% of an acid. The pH of the bath is immaterial. In the presence of acid the HCHO forms a 2:4-diamino-formaldehyde complex with the residual developer which complex is readily removed by rinsing with water.
C. O. C.

Ceramic Articles with Tinted or Coloured Reproductions in Recess. J. M. M. Bach. *BP* 717,879

A sheet of gelatin or gelatin-containing material is photosensitised with an aqueous solution of a dichromate and then dried. The sensitised sheet is pressed against a photographic negative or diapositive of the picture or pattern to be reproduced and is exposed to light for the equivalent of 1–5 hr. of sunlight. The exposed sheet is then soaked in water at 30°c. for 1–6 days until the gelatin swells to an extent inversely dependent on the intensity of the light to which it has been exposed and forms on its surface an exact reproduction in recess of the pattern. On air drying this shallow recess pattern remains in the sheet. The sheet is now immersed in a dilute suspension of a colouring matter and is removed after some of the colouring matter has settled on it. The colouring matter settles more in the recesses than on the other parts and so by using the coloured sheet as a mould for making a ceramic article an exact reproduction of the pattern is obtained on the resulting ceramic article.
C. O. C.

Electrostatic Coating (I p. 53).
Light-responsive Fluorescent Media (V p. 61).
Printing Inks for Application to Plasticised Polyvinylbutyral Sheets in Dyeing such Sheets (V p. 61).
Level Dyeing or Printing of Nylon (VIII p. 65).
Transfer Coating (X p. 68).

X—SIZING AND FINISHING

Extensive Amination of Cotton with Ethyleneimine. L. M. Soffer and E. Carpenter. *Text. Research J.*, **24**, 847–852 (Sept. 1954).

Aminated cottons of nitrogen contents ranging up to 29% are prepared by heating chemical cotton with ethyleneimine at 140–130°c. A possible chemical structure for the products is discussed.
A. B.

Effect of Time and Temperature of Presoaking and the Temperature of Acetylation on the Rate and Degree of Acetylation of Cotton Fibres. J. L. Taylor and E. D. Owens. *Text. Research J.*, **24**, 810–819 (Sept. 1954).

A study is made of the effects of the time and the temperature of presoaking on the rate and the degree of acetylation of different varieties of cotton fibres with the time and temperature of the acetylation held constant, and also of the effect of the temperature of acetylation on the degree of acetylation under constant conditions of presoaking. Optimum conditions for acetylation are determined.
A. B.

Resistance of Partly Acetylated Cotton Fabric to Nitrogen Dioxide and to Hydrogen Chloride. W. T. Schreiber, A. L. Bullock, and W. L. Ward. *Text. Research J.*, **24**, 819–822 (Sept. 1954).

It is shown that partly acetylated cotton is resistant to mixtures of nitrogen dioxide and air and to hydrogen chloride, as compared with ordinary bleached cotton. This is demonstrated using data on breaking strength,

cuprammonium fluidity, carboxyl content, and copper number. Possible explanations for this resistance are discussed. A. B.

Weathering Characteristics of Cotton Fabrics containing Inorganic Compounds. I—Chromic Oxide and Copper in Inorganic and Organic Forms. G. R. F. Rose and C. H. Bayley. *Text. Research J.*, **24**, 792–802 (Sept. 1954).

It is shown that chromium and copper in inorganic form confer marked protection against actinic breakdown of cellulose, and also prevent the severe loss of copper which occurs in the absence of chromium during weathering. These effects also occur to a lesser degree with chromium-treated fabrics aftertreated with copper-containing organic fungicides. Lightweight fabrics treated with mixtures of inorganic chromium and copper showed resistance to actinic degradation, but underwent severe loss of copper. A. B.

Modification of Wool by the Application of Linear Synthetic Polyamides. V—Pretreatment with Ethanolic Potassium Hydroxide. J. Delmenico, D. L. C. Jackson, and M. Lipson. *Text. Research J.*, **24**, 828–834 (Sept. 1954).

It is shown that the felting of wool may be eliminated by treatment with extremely low concentrations of alkoxymethylpolyamide resins if either wool is first treated with alcoholic potash solutions, with or without subsequent neutralisation, or the alkali is incorporated in the alcoholic resin solution. A. B.

PATENTS

Heat Stabilised Cellulose Yarn. DuP. *USP* 2,653,112

Cellulose is stabilised against degradation by heat by impregnating it with a metal, e.g. Al or Mg, which at 150°c. forms alkaline products with air and water. Regenerated cellulose thread impregnated with 0·2% of flake Mg on heating for 4 hr. at 150°c. in a sealed tube containing air and 12% moisture lost 14% in strength whereas an untreated thread lost $> 50\%$ in strength. C. O. C.

Protecting Cellulose against Thermal Degradation. United States Rubber Co. *USP* 2,650,891

Water-soluble 2:2′-diaminodialkyl sulphides are highly effective for imparting to cellulose ability to withstand degradation when exposed to heat for prolonged periods. C. O. C.

***N*-Halogenated Amine–Aldehyde Condensates for Imparting Crease Resistance and Dimensional Stability.** Monsanto. *USP* 2,654,720

Use of water-soluble *N*-halogenated melamine- or urea-formaldehyde condensates imparts crease resistance, dimensional stability and a soft, full, natural handle. C. O. C.

Rendering Fabrics Dimensionally Stable. E–Z Mills. *USP* 2,655,711

The completely wet fabric is relaxed, preferably by spreading it under the surface of an aqueous liquid so that the weight of the fabric is compensated by its buoyancy and the friction of the water is applied to the fabric on a surface many times greater than the acting surfaces of the rollers of a conventional spreader. An A.C. current is then passed through the fabric, while it is still relaxed and retaining at least some of the liquor from the bath, to cause internal heating dielectrically until the fabric is dry. C. O. C.

Flame-resistant Finish for Cellulosic Materials. National Lead Co. *USP* 2,658,000

The material is impregnated with an aqueous solution of titanium chloride acylate* which is then gelatinised to form a transparent gel and the impregnated material treated with an alkaline neutralising agent, washed and dried. Best results are produced when the fabric takes up 6–9% of its dry weight of the acylate. The afterglow resistance can be increased by addition of antimony chloride. The finish is fast to washing. C. O. C.

* Formate, acetate, etc.

Reducing the Felting Power of Wool. Stevensons (Dyers). *BP* 716,806

The material is first treated with aqueous permonosulphuric acid or a permonosulphate at pH < 8 and then with an aqueous solution or dispersion of sulphurous acid or a sulphite. C. O. C.

Permanent Waving of Hair. E. O. Schnell. *USP* 2,653,121

An aqueous solution of calcium thioglycollate and an acidic ammonium salt, whose anion forms water-soluble NH_4-salts, is a good permanent waving preparation requiring no neutralising or oxidising aftertreatment. It is applied at pH 9·2–9·5 and after application the pH steadily falls, the operation being complete when pH 5 is reached. C. O. C.

Hardening of Films or Fibres of Non-cellulosic Hydrophilic Polymers. Bradford Dyers' Association. *BP* 716,542

Films or fibres of non-cellulosic hydrophilic polymers, e.g. proteins, polyvinyl alcohol, alginates or polyacrylates, are hardened or insolubilised by treating them with the reaction product of an alkali metal bisulphite with a mono- or polyfunctional organic *iso*cyanate or *iso*thiocyanate and then baking at a temperature at which the bisulphite-cyanate compound decomposes. C. O. C.

Siloxane-coated Textiles. Dow Corning. *BP* 717,638

A dyed organic textile on which has been deposited a coating made up of (*a*) 100 parts by wt. of a benzene-soluble organosiloxane polymer whose structural units are of formula $R_{2n}SiO_{1-n}$ (R = CH_3, C_2H_5 or C_6H_5; n = 0·925–1·025) and (*b*) 20–80 parts of a silica filler of pore volume < 3 c.c./g. and a heat of wetting, measured in hexamethyldisiloxane, of 0·1–1·8 cal./c.c. of pore volume. This gives protection against fading caused by ultraviolet radiation. In addition, the treated textiles are waterproof, water-repellent and stain-resistant without noticeable effect on their handle. C. O. C.

Improving the Wear Resistance of Fibrous Materials. Société pour le Traitement et l'Amélioration des Tissus. *BP* 717,144

The material is impregnated with a silicic acid ester containing only ester groups attached directly to Si, e.g. ethyl silicate, and is then heated to decompose the ester and fix silica in the fibres. C. O. C.

Water-repellent Finish. Basf. *BP* 717,624

Fibrous materials are given an excellent hydrophobic finish by impregnating them with mixtures of (*a*) interpolymers of vinyl ethers of hydroaromatic alcohols and olefins containing > 4C and an *iso*propylidene group, and (*b*) wax or fat. C. O. C.

Rotproofing. Deutsche Gold- und Silber-Scheideanstalt. *BP* 717,557

Impregnation with zinc thiocyanate gives excellent and lasting protection against attack by micro-organisms. When used in high concentrations it also imparts an excellent flame-resistant finish. C. O. C.

Coated Knitted Fabric. ICI. *BP* 717,602

A warp knitted material reinforced at intervals across its width by warp yarns of greater tensile strength than the others is coated with a plastic or elastic material, e.g. polyvinyl chloride, cellulose nitrate or rubber. This yields a fabric of relatively low extensibility and a high tear strength both warp and weft ways. C. O. C.

Setting Protein-containing Coatings with Ammonia. Eastman Kodak Co. *USP* 2,652,345

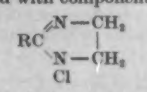
Cloth, paper, etc. are coated with an aqueous protein composition containing HCHO, acrolein or glyoxal and then immediately treated with gaseous ammonia. This causes almost instantaneous setting of the coating. C. O. C.

Coated Polyester Fabrics. ICI. *BP* 718,218

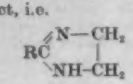
Terylene fabrics are coated with a solution of a polyhydric alcohol–polybasic acid condensate and an organic poly*iso*cyanate, after which the solvent is removed and the fabric heated. The coating is free from cracking or crazing even if creased at very low temperatures and the creases are readily removed by ironing. C. O. C.

Gas-protective Fabric. U.S. Secretary of War. *USP* 2,659,681

Fabric impregnated with components of formula—



(R = hydrocarbon or hydroxyhydrocarbon radical of a fatty acid), gives good protection against mustard gas or the like. If desired, the fabric can be impregnated with the unchlorinated product, i.e.



and the fabric then put into store or into use. Later on the impregnated fabric can be chlorinated, e.g. by treatment with aq. sodium hypochlorite to bring its anti-vesicant properties into use. C. O. C.

Transfer Coating. Minnesota Mining & Manufacturing Co. *USP* 2,658,007

A method whereby each particle of the coating material is positively held in a precise predetermined position during the coating operation. C. O. C.

Pile Fabrics. Dunlop. *BP* 716,311

Pile fabrics are made by applying to a non-woven sheet or film of a polymer or copolymer of vinyl chloride, a polymer or copolymer of vinyl chloride dispersed in a suitable plasticiser, e.g. dioctyl phthalate, along with a stabiliser, e.g. $PbCO_3$, and distributing thereon fibres in pile fashion. This assembly is heated to gel the paste. If it is desired to make a foam paste a blowing agent, e.g. dinitrosopentamethylene tetramine, is included. J. W. B.

Soil-resistant Pile Fabrics. Mohawk Carpet Mills. *BP* 718,250

Pile fabrics whose pile contains $> 20\%$ of vegetable and/or synthetic fibre is coated with 0·15–0·50 oz. per sq. yd. of colloidal silica on the exposed portion of the pile. The treated fabric does not readily become dirty. C. O. C.

Glazing Batting Materials containing Organic Thermoplastic Fibres. Celanese Corpn. of America. *BP* 718,529

Batting containing organic thermoplastic fibres has its surface treated with an aqueous solution or dispersion of a softening agent of b.p. $> 125°$c. and is then treated with a hot surface so as to coalesce the surface fibres. C. O. C.

N-Acylamino Mercaptans—Agents for Setting Proteinaceous Materials (III p. 54).

Coatings of Polyamide and Epoxy Resin Blends (V p. 61).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Preparation of Cellulose III with Ethylamine. L. Segal. *Text. Research J.*, **24**, 861–862 (Sept. 1954).

A comparison is made between the work carried out by Mann and Marrinan (*Chem. and Ind.*, 1092 (1953)) on the treatment of cellulose with ethylamine and the work of the present author, and differences in the results are discussed. A. B.

Synthesis and Reactions of Vinyl Ethers of Higher Polyhydric Alcohols and Cellulose. Tetravinyl Ether of Methyl α-Glucoside. M. F. Shostakovskiĭ, E. N. Prilezhaeva, and L. V. Tsŷmbal. *Doklady Akad. Nauk S.S.S.R.*, **96**, 99–102 (1 May 1954).

The unsatisfactory results of previous attempts to prepare vinyl ethers of cellulose and of polyvinyl alcohol are discussed, and it is suggested that to prevent the side-reactions that readily occur owing to the tendency for partial ethers to undergo cyclisation reactions, it is essential to provide conditions for rapid and exhaustive vinylation. This supposition is tested by experiments on methyl α-glucoside, taken as a model substance to represent the unit of a cellulose chain, and it is found that vinylation in dioxan soln. by means of acetylene (3- to 4-fold excess) in presence of KOH at 125–145°c. for 11 hr. gives an 85% yield of the tetravinyl ether. A. E. S.

PATENTS

Porous Fibrous Web Material. C. H. Dexter & Sons. *BP* 715,932

Preparation of a thin, soft, highly absorbent and porous web material of low density comprises forming a highly dilute (1 in 5,000–10,000) aqueous slurry of unbeaten, synthetic fibres of length from 6 mm. to that of textile fibres with addition of a small quantity of water-dispersible sodium carboxymethylcellulose (1 part by weight to 5–25 parts of fibre) to disperse the water-soluble content and deflocculate the fibre in the suspension and the water-insoluble particles binding the fibres at their intersections in the finished sheet. A web is formed by flowing the dispersion on to a travelling meshed sheet-forming screen to cause the fibres and the gel particles of sodium carboxymethylcellulose adhering to the intersections of the fibre to deposit uniformly thereon while permitting the remainder of the slurry to flow through the screen, and drying the web to cause the gel to bind the fibres. S. V. S.

Water-resistant Coatings for Paper. Calgon. *USP* 2,652,374

In coating compositions containing starch and a urea-formaldehyde resin use of NH_4PO_3 as the catalyst avoids any increase in viscosity of the coating slurry. C. O. C.

Incorporating Particles of an Inorganic Substance into Paper. National Cash Register Co. *BP* 717,805

In impregnating with a normally colourless inorganic substance, paper sheets are successively treated with solutions that interact to precipitate a silicate in, around and between the fibres, capable of producing a colour reaction when brought into contact with a colourless marking substance containing a colour reactant material. The successive aqueous solutions may be of a salt of magnesium, aluminium, mercury, zinc, calcium, barium, strontium, lead, manganous manganese or tin, and of a silicate compound, which may contain a latex, e.g. an anionic butadiene–styrene copolymer in 1% concentration by weight. Excess of first reagent solution may be removed before the second is applied. Either solution contains a soluble oxidising salt, e.g. sodium chlorate, to assist in oxidising absorbate marking substances when applied to the finished paper. S. V. S.

Decalcomania Paper. McLaurin-Jones Co. *BP* 717,079

A decalcomania paper, comprising a sized-paper backing sheet and a coating of adhesive material adapted to carry decalcomania printing, is dry and non-tacky under normal humidity conditions, and the firmly-united coating is readily released from the backing sheet when immersed in water, and contains dimethylhydantoin (5–80% by weight of the dry coating), and sodium cellulose sulphate (5–25%). S. V. S.

Light-sensitive Materials and Surfaces for the Reception of the same. H. P. Andrews Paper Co. *BP* 717,835

A surface for receiving a light-sensitive compound is prepared by applying a binder-free water dispersion of water-insoluble synthetic resin particles to the surface of a fibrous base material, e.g. paper, and drying the dispersion on the paper, which may have been sized to restrict penetration by a sensitising solution. A layer of light-sensitive material, e.g. a diazo compound, is then applied to the paper with its discontinuous layer of discrete resin particles. S. V. S.

Photographic Backing Paper. Kodak Limited. *BP* 717,926

An optically opaque photographic backing paper having an overall thickness of less than 0·004 in. comprises a single sheet of paper having a black pigment coating on one side, the other side having a lighter coloured pigment applied. The black pigment may be carbon black and the lighter coloured coating made up of 2 strata, the first (nearest the sheet) containing a white pigment, e.g. titanium dioxide and the second containing a lighter coloured pigment which may be yellow or blue. The second stratum may contain titanium dioxide, chrome yellow pigment and a light orange pigment and the lighter

side may be printed upon, afterwards being overcoated with a prolamine such as zein. The paper itself may be coloured yellow by means of a yellow pigment or black with carbon black and the uncoated side may be printed upon and may be kraft paper of 14 lb. per thousand sq. ft. having a thickness of less than 0·003 in. before coating.

BP 717,958

An optically opaque photographic backing paper, having an overall thickness of less than 0·004 in., comprises a single sheet of paper 0·0025–0·0032 in. thick having a black pigment coating on one side consisting of two strata, the first (nearest the paper) containing black pigment in a soft resin binder, and the second black pigment in a zein binder, the paper having a lighter coloured pigmented coating on the other side. S. V. S.

Modifying and Converting Starch (III p. 54).

Coatings of Polyamide and Epoxy Resin Blends (V p. 61).

Recording Paper to be marked by Electrical Means (IX p. 66).

Manifolding Transfer (IX p. 66).

Hardening of Films or Fibres of Non-cellulosic Hydrophilic Polymers (X p. 67).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Peptide Complexes with Zinc and Cadmium Ions in Aqueous Solution. D. J. Perkins. *Biochem. J.*, **57**, 702–704 (Aug. 1954).

Zinc and cadmium complexes of peptides have lower stability constants than the corresponding complexes of free amino acids. Examination of the homologous peptide series glycine–triglycylglycine shows that complex stabilities decrease further with the introduction of the first and second peptide bonds but increase slightly with the third. The order in which the amino acid residues of the peptide occur is shown to be important. The glycyl peptides of a number of amino acids have complex stability constants which can be roughly predicted from their amino acid content. P. G. M.

Contraction and Relaxation of Collagen Fibres. I. Banga, J. Baló, and D. Szabó. *Nature*, **174**, 788–789 (23 Oct. 1954).

N-Terminal Amino Acid Residues of Gelatin. I—Intact Gelatins. II—Thermal Degradation. A. Courts. *Biochem. J.*, **58**, 70–74; 74–79 (Sept. 1954).

I—The *N*-terminal residues of a number of gelatins have been determined using Sanger's fluorodinitrobenzene technique. Glycine was found to be the predominant end-group. Serine, threonine, alanine and aspartic and glutamic acid residues also occurred. The number-average molecular weight of these samples was calculated assuming one *N*-terminal residue in each molecule. Average values of 60,000 were in agreement with those obtained by osmotic-pressure methods and support the view of a non-branching peptide chain. The method has been used to determine the lysine residues of gelatin. Generally, over 90% of the ε-amino groups of lysine were available to the reagent.

II—The *N*-terminal residues formed during degradation of gelatin under various conditions have been studied. It is shown that the relative lability of different types of peptide bond varies with the pH of degradation. The mean activation energy for peptide-bond hydrolysis at pH 5·1 is calculated as 18,960 cal./mole. The extent of degradation, as measured by *N*-terminal residues, is compared with values obtained viscometrically. The kinetics of peptide-bond hydrolysis are discussed in relation to certain previous work. P. G. M.

PATENTS

Tanning Materials. Standard Dyewood Co.

USP 2,653,067

When natural tannins, particularly quebracho extract, are bleached with use of a vanadium compound as catalyst the products produce much lighter leather than do those bleached in absence of vanadium. C. O. C.

Coating Compositions for Leather. Basf. *BP* 717,883

A colloidal solution of an ammonium salt of a carboxyl group-containing copolymer of an acrylic or methacrylic ester in an aqueous organic solvent is an excellent coating agent for leather. The coatings obtained have very good glazing properties. C. O. C.

XIII—RUBBER; RESINS; PLASTICS

Effect of Pressure on the Polycondensation of the Methyl Ester of Glycine. A. M. Polyakova, L. F. Vereshchagin, A. A. Sakharova, and E. S. Tambovtseva. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 142–148 (Jan.–Feb. 1954).

In the polycondensation of glycine methyl ester, application of high pressure (4500 atm.) leads to higher yields of polymer (yield increased from 4% to 13% at 75°C.) and to higher mol.wt. (increased from 1460 to 3860 at 75°C.). With rise in temp. the yield rises, but the mol. wt. falls. No solvent was found for the polymer, and the mol.wt. is determined from methoxyl and amine end-group determinations, which are in close agreement. An electrolytic reduction test is negative, indicating absence of piperazine-2:5-dione residues. The polymer is considered to be linear. A. E. S.

Macromolecular Compounds. LXIV—Polycondensation of the Ethyl Ester of DL-Alanine. V. V. Korshak, K. T. Poroshin, and T. D. Kozarenko. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk*, 663–669 (July–Aug. 1954).

The polycondensation of DL-alanine ethyl ester is accelerated by acids, but not by bases. The kinetics of the reaction are studied, with and without catalyst (carbon dioxide, acetic acid, and polyalanine); formation of linear polymer to the exclusion of cyclic dimer is favoured by low temperature. Copolymerisation of the ethyl esters of DL-phenylalanine and phenylglycine (each of which gives insol. polymers) yields a water-sol. product. A. E. S.

PATENTS

Rubber Antioxidants. Monsanto. *BP* 717,863

A mixture of a 2:4:6-trialkylphenol and a mono-ether of a dihydric phenol is an effective antioxidant for vulcanised rubber and is especially suitable for use in light coloured stocks. C. O. C.

Rendering Polyethylene receptive to Printing Ink. M. F. Kritchever. *BP* 718,715

Polyethylene is made highly receptive to printing inks by directing a gas flame on to it without raising it to a temperature enabling distortion. C. O. C.

Organo-tin Stabilisers for Polyvinyl Chloride or Polyvinylidene Chloride. B. F. Goodrich Co. *BP* 717,973

Compounds of formula—

$$R^1R^2SnO$$

(R^1 and R^2 = same or different monovalent hydrocarbon groups) e.g. dimethyl tin oxide or phenylbutyl tin oxide, stabilise vinyl and vinylidene chloride polymers to heat and light. C. O. C.

Stabilisers and Plasticisers for Vinylidene Chloride Polymers and Copolymers. Distillers Co. *BP* 717,841

Di-esters of α-methylbenzyl alcohol with benzene or naphthalene dicarboxylic acids or nuclear chloro substituted derivatives thereof, carbonic acid, oxalic acid, straight chain $\alpha\omega$-dicarboxylic acids of formula HOOC·$[CH_2]_n$·COOH (n = 2–8), maleic or fumaric acid are both plasticisers and stabilisers to light for vinylidine chloride polymers and copolymers. C. O. C.

Blending Incompatible Synthetic Resins. Visking Corpn. *USP* 2,658,051

Polychloroprene and vinylidene chloride–acrylonitrile copolymers are rendered compatible by mixing them with a 1:3-butadiene–acrylonitrile copolymer.

USP 2,658,052

Polyvinylidene chloride and a butadiene–acrylonitrile copolymer are rendered compatible by mixing them with polyvinyl chloride or a vinyl chloride–vinyl acetate copolymer.

USP 2,658,053

Vinyl chloride–vinylidene chloride copolymers and butadiene–acrylonitrile copolymers are rendered compatible by mixing them with polychloroprene. C. O. C.

Luminescent Resins from Aryl-substituted Alkyl Halides and Alkenyl Ethers of a Polyhydroxy Organic Compound. Universal Oil Products Co. *USP* 2,654,732

Fluorescent resins are obtained by condensing an aryl-substituted alkyl halide, e.g. an *αα'*-dichloroxylene, with an alkenyl ether of a polyhydroxy organic compound, e.g. a glycerol-*α*-alkyl ether, in presence of aqueous alkali. They are pale yellow to red, dry oil resins suitable for use in paints, printing inks, etc. to yield clear, lightly coloured, tough, transparent coatings which emit fluorescence from an edge of the film or from various points on the film's surface. C. O. C.

Stable Coloured Dioxan–Water Solutions. Monsanto. *USP* 2,657,970

Addition of diethylaminoethanol stabilises solutions of oil-soluble dyes in a mixture of dioxan and water against atmospheric oxidation. Such solutions are used for dip staining thermoplastic sheets either to overcome their natural yellowness or to colour them. C. O. C.

Printing Inks for Application to Plasticised Polyvinyl-butyral Sheets in Dyeing such Sheets (V p. 61).

Macromolecular Compounds. LXIII and LXVI— Heteropolymerisation of Di*iso*cyanates and Glycols (VI p. 62).

XIV— ANALYSIS; TESTING; APPARATUS

Modified Liquid–Liquid Extractor for Routine Oil Analysis. C. R. Buerki and K. E. Holt. *J. Amer. Oil Chem. Soc.*, **31**, 335–338 (Aug. 1954).

A continuous liquid–liquid extractor was designed and procedures were devised for the determination of total fatty acids, oxidised acids, and unsaponifiable matter. These procedures give results that are in agreement with the present American Oil Chemists Society methods. P. G. M.

Polarographic Determination of Titanium in Soap. J. Hejna. *J. Amer. Oil Chem. Soc.*, **31**, 350–352 (Aug. 1954).

A polarographic method is given by which titanium dioxide can be determined in soaps. It was found that no maximum suppressor was necessary and that the diffusion current is directly proportional to the concentration and is well defined. P. G. M.

Paper Chromatography of Coal-tar Colours. D. H. Tilden. *J. Assocn. Off. Agric. Chem.*, **37**, 812–817 (1954): *Chem. Abs.*, **48**, 11790 (10 Oct. 1954).

Two soln.— one of FD&C Yellow No. 5, Green No. 2, and Orange No. 1; the other of FD&C Red No. 2, Yellow No. 5, Blue No. 1, and Orange No. 1— were correctly resolved by five different workers by paper chromatography. A soln. of FD&C Red No. 1, Red No. 2, Yellow No. 6, and Orange No. 1 was correctly resolved by four of the workers, but the fifth could identify only three of the dyes. C. O. C.

Separation of Triphenylmethane Food Colours by Column Chromatography. G. G. McKeown and J. L. Thomson. *J. Assocn. Off. Agric. Chem.*, **37**, 917 (1954): *Chem. Abs.*, **48**, 11665 (10 Oct. 1954).

The five triphenylmethane dyes permitted for food use in Canada and the U.S.A.— Brilliant Blue FCF (FD&C Blue No. 1), Light Green SF Yellowish (FD&C Green No. 2), Fast Green FCF (FD&C Green No. 3), Guinea Green B (FD&C Green No. 1), and Benzyl Violet 4B (FD&C Violet No. 1)— are adsorbed from acid solution as lakes on an alumina column. The column is developed with weakly basic solutions. With 1·0–1·5% pyridine soln., binary mixtures with the exception of FD&C Green No. 2 and FD&C Green No. 3, and FD&C Green No. 1 and FD&C Blue No. 1, can be resolved and the components determined spectrophotometrically. C. O. C.

Subsidiary Dyes in FD&C Colours. I— Higher Sulphonated Dyes in FD&C Yellow No. 6. M. Dolinsky. *J. Assocn. Off. Agric. Chem.*, **37**, 805–808 (1954); **II— Subsidiary Dyes in FD&C Red No. 2.** *Ibid.*, 808–812: *Chem. Abs.*, **48**, 11665 (10 Oct. 1954).

I— Presence of the 2-naphthol-3:6-disulphonate and 2-naphthol-6:8-disulphonate analogues of FD&C Yellow No. 6 (disodium 1-sulphophenylazo-2-naphthol-6-sulphonate) in the commercial dye is detected by extracting the dye with *iso*pentyl alcohol from solution in dil. HCl and determining the absorbance in the acid soln. at 490 mμ. and 476 mμ. for the two disulphonates respectively. A number of commercial samples of the dye contained 0·1–6·0% of the disulphonates, mainly the first one.

II— It is confirmed that the former A.O.A.C. method for determining *C.I.*182 in FD&C Red No. 2 (*A.O.A.C. Methods of Analysis* (6th edition (1945)) is effective. The method given for determining *C.I.*185 in FD&C Red No. 2 is suitable for rapid approximation. *C.I.*185 can be determined quantitatively by chromatography on powdered cellulose using 3% brine as the eluant. *C.I.*182 does not interfere. Five commercial samples of FD&C Red No. 2 contained 0·2–0·7% of *C.I.*182 and < 0·3% of *C.I.*185. C. O. C.

Subsidiary Dyes in D&C Colours. 4-Tolylazo-2-naphthol in D&C Red No. 35. L. Koch. *J. Assocn. Off. Agric. Chem.*, **37**, 803–805 (1954): *Chem. Abs.*, **48**, 11791 (10 Oct. 1954).

The Graichen and Harrow spectrophotometric procedure for determining 4-tolylazo-2-naphthol in D&C Red No. 35 is more accurate than the chemical method previously studied. C. O. C.

Coal-tar Colours. XVI— FD&C Red No. 4. C. Graichen and K. S. Heine. *J. Assocn. Off. Agric. Chem.*, **37**, 905 (1954); **XVII— Ext. D&C Red No. 1.** R. N. Solar and K. A. Freeman. *Ibid.*, 1913: *Chem. Abs.*, **48**, 11791 (10 Oct. 1954).

XVI— Pure samples were prepared of FD&C Red No. 4 (disodium 2-(5-sulpho-2:4-xylylazo)-1-naphthol-4-sulphonate) and of its isomer (the 6-sulpho derivative). Chromatographic, ultraviolet, visible, and infrared spectrophotometric data are given of the two dyes and of the purified intermediates used to make them. These data, the variable-reference spectrophotometric titration, and the $TiCl_3$ titration were used in the analysis of six commercial samples of FD&C Red No. 4, and all proved to be essentially pure.

XVII— Pure D&C Red No. 11 (aniline→acetylated H acid) was prepared and analysed, and its spectrophotometric properties were measured. Impurities which commercial samples may be expected to contain are— Acid Fuchsin D, Ext. D&C Red No. 33, aniline→H acid, and Chromotrope 2R. The commercial dye is most conveniently freed from these impurities by cellulose column chromatography. Four commercial samples contained 0·9–2·0% of Acid Fuchsin D and < 0·5% of Chromotrope 2R. C. O. C.

Report on Hair Dyes and Rinses. Analysis of Mixtures of *p*-Aminophenol and *p*-Phenylenediamine or 2:5-Diaminotoluene. S. H. Newburger and J. H. Jones. *J. Assocn. Off. Agric. Chem.*, **36**, 784–789 (1953): *Chem. Abs.*, **48**, 10303 (10 Sept. 1954).

Mixtures of *p*-phenylenediamine or 2:5-diaminotoluene with *p*-aminophenol, quantitatively extracted with ether from conc. salt soln. buffered with $NaHCO_3$, were spectrophotometrically analysed with reasonable accuracy. C. O. C.

Interaction of Dyes with Proteins on Paper with special reference to Paper Electrophoresis. G. F. Franglen and N. H. Martin. *Biochem. J.*, **57**, 626–630 (Aug. 1954).

The spectral absorption characteristics of Bromophenol Blue, Bromocresol Green, Azocarmine B, and Naphthalene Black 12B have been examined. Azocarmine B is heterogeneous on chromatography on filter paper. The dye-binding characteristics of human albumin and human *γ*-globulin with Bromocresol Green have been studied individually and in mixtures of known composition. The

results suggest that existing quantitative methods of analysis by paper-strip electrophoresis require reassessment. P. G. M.

Detection of Iron and Gallic Acid in Writing Ink. T. Kurita. *Japan Analyst*, **3**, 135–136 (1954): *Chem. Abs.*, **48**, 10355 (10 Sept. 1954).

Strips of filter paper are used, impregnated with a saturated solution of dimethylglyoxime in acetone and dried. A strip dipped into the sample and then immediately dipped into ammonia shows bright red at the top of the dyed pattern if Fe is present. 2–3 drops of the sample are mixed with 0·4–0·5 g. NaCl and the mixture is allowed to ascend 2·3 cm. up a strip. If Fe is present, the leading edge of the ascending mixture turns violet blue. If gallic acid is present, there are light black and light yellow zones which turn red and violet black when treated with ammonia. C. O. C.

Iodine Adsorption as a Measure of Cellulose Fibre Crystallinity. L. E. Hessler and R. E. Power. *Text. Research J.*, **24**, 822–827 (Sept. 1954).

The iodine adsorption method is shown to be useful in detecting changes in the crystallinity of cotton cellulose. Differences in cellulose crystallinity due to fibre development are demonstrated. This method shows good agreement with the results of other chemical methods for determining crystallinity. A. B.

Determination of Microcrystallite Size in Rayons. A. N. J. Heyn. *J. Polymer Sci.*, **14**, 403–404 (Oct. 1954).

It is suggested that swelling in water does not fully eliminate interparticle interference in the determination of particle size by techniques based on the small-angle scattering of X rays. Swelling under carefully controlled conditions may make determination possible. W. R. M.

Practical Applications of a Method for the Differential Coloration of Viscose Rayon. N. Iwanow, R. Schneider, and J. Meybeck. *Bull. Inst. Text. France*, (48), 49–59 (Aug. 1954).

The method (*ibid.*, (35), 51 (1952)) reveals small differences in the quality of viscose rayon filament and staple and permits these to be estimated quantitatively, but the laboratory findings cannot readily be related to practical results. Statistical treatment of the test data may be used for production and process control. S. R. C.

Standard I.W.T.O. Method for the Determination of the Ether Extract of Worsted Slubbing. International Wool Textile Organisation. *Bull. Inst. Text. France*, (48), 77–79 (Aug. 1954).

Estimation of the Ether Extract of Wool. M. Robinet. *Bull. Inst. Text. France*, (48), 81–86 (Aug. 1954).

A description of development and inter-laboratory work and of the Barritt–Elsworth modification leading to the I.W.T.O. Standard (see previous abstract). The usefulness is discussed of testing for complete degreasing by evaporation on a water-bath, and the necessity is stressed of evaporating the ether solution by direct heat from a boiling water-bath, in order to expel water dissolved in the ether. S. R. C.

Simple Method for the Separation of Amino Acids by Partition Chromatography on Paper. N. M. Sisakyan, E. N. Bezinger, P. G. Gavkavi, and G. Ya. Kivman. *Doklady Akad. Nauk S.S.S.R.*, **96**, 343–346 (11 May 1954).

In two-dimensional paper chromatography of a protein hydrolysate, methanol–water–pyridine (40 : 10 : 2) is taken as first solvent and 1-butanol–2-butanone–water–diethylamine (20 : 20 : 10 : 2) is taken as second. Development with 0·4% methanolic ninhydrin is preceded by treatment in steam for 5 min. to remove diethylamine. The use of the method to separate twenty amino acids is described. The method is rapid, and has also other advantages over known methods; thus, cystine and methionine, which cannot be estimated directly when a phenol is used as solvent, are readily determined. A. E. S.

Determination of the Intrinsic Viscosity of Polyethylene Terephthalate Solutions. H. Frind. *Faserforsch. und Textiltech.*, **5**, 290–296 (July 1954).

A suitable solvent for the determination of the intrinsic viscosity of polyethylene terephthalate solutions is a 1 : 1 mixture of phenol and tetrachloroethane. At 80°c. solution is complete in < 30 min., and no polymer degradation occurs in this process; the results are insensitive to small changes in the ratio of solvent components. Measurements made with an Ubbelohde dilution viscometer on four samples of polyethylene terephthalate varying widely in degree of polymerisation indicate that η_{sp}/c (η_{sp} = specific viscosity; c = concn.) passes through a min. at $c = \sim 0{\cdot}1$ g./100 c.c. (below this concn. the effect of polymer–solvent interaction becomes predominant), and that above this concn. it may be expressed by the linear relation—

$$\frac{\eta_{sp}}{c} = [\eta] + 0{\cdot}35[\eta]^2c$$

from which the intrinsic viscosity $[\eta]$, and hence the mean mol.wt. of the polymer, can be calculated, a single measurement of η_{sp} at a suitable concn. being in many cases sufficient for this purpose. A. E. S.

Assessment of Chemical Damage to Cellulosic Textiles during Industrial Bleaching. A. Parisot and A. Fresco. *Bull. Inst. Text. France*, (48), 7–48 (Aug. 1954).

Where cellulosic textiles undergo repeated launderings with the minimum of intermediate wear (e.g. hotel linen), the degree of polymerisation (D.P.) of the cellulose varies hyperbolically with the number of washings; i.e. the rate of degradation rate is constant. The reciprocal of the D.P. varies linearly with the difference between the wet (W) and dry (D) bursting strengths. With most fabrics composed of native cellulose, when $W = D$, D.P. = 600–700, and the useful life of the textile is finished. S. R. C.

Thermostat Cell-holder for the Beckman Spectrophotometer. M. Dixon. *Biochem. J.*, **58**, 1–3 (Sept. 1954).

The temperature of the cells is held constant by water circulating in contact with them. This gives rapid equilibration and accurate control. P. G. M.

Measurement of Translational Diffusion Coefficients. T. J. Bowen. *Lab. Practice*, **3**, 369–373 (Sept.), 414–417 (Oct. 1954).

Methods for the measurement of diffusion in soln. are described. The theory of the methods is outlined, and the apparatus used is illustrated. There are 74 references. A. E. S.

Application of Radiochemical Techniques to the Study of the Interaction of Hair Fibres with Aqueous Solutions. P. B. Stam and H. J. White. *Text. Research J.*, **24**, 785–791 (Sept. 1954).

Radioactive tracer techniques have proved to be uniquely adaptable to the study of the interaction of hair fibres with various aqueous solutions including dyebaths. Observations were made on NaBr, NaBr–HBr, and NaCl soln., and in a preliminary experiment the absorption of each of three components of an acid dyebath was followed by taking advantage of differences in radioactive behaviour of the three species. A. B.

Determination of Chlorine in Pentachlorophenol and Pentachlorophenol Laurate. E. H. Searle and E. Bell. *J. Appl. Chem.*, **4**, 430–433 (Aug. 1954).

A method for the determination of chlorine in pentachlorophenol and pentachlorophenol laurate is given, and it is applied to the estimation of polychlorinated phenols in textiles— The textile (2 g.) is oven-dried and then refluxed for 1 hr. with tetrahydrofurfuryl alcohol (10 ml.). The soln. is cooled to 80°c., and 5 ml. is transferred to a tube, in which it is simmered with KOH (0·6–0·8 g.) for 30 min. The alcohol is then distilled off, and heating is continued until thick white fumes fill the condenser. The mass is dissolved in water, the soln. is acidified with nitric acid to pH 1·0, the tar that separates is filtered off and washed, and chloride is estimated in the filtrate and washings. A. E. S.

Detection and Estimation of Melamine in Wet-strength Paper by Ultraviolet Spectrophotometry. R. C. Hirt, F. T. King, and R. G. Schmitt. *Anal. Chem.*, **26**, 1273–1274 (Aug. 1954).

The resin is removed from the paper and hydrolysed by refluxing with 0·1 N-HCl, and the estimation is based upon the strong absorption of the melamine ion near 235 mμ. Other ultraviolet-absorbing materials may also be extracted, and the absorption at 260 mμ. may be subtracted from the reading at 235 mμ. as a preliminary correction for the background effect. By the use of 237 mμ. instead of 235 mμ. as the absorptive wavelength, any error due to the presence of ammeline (I) is avoided, melamine (II) and I having an iso-absorptive point at this wavelength, and the two compounds may be jointly assayed as II. The max. at 235 mμ., observed in HCl soln., disappears in alkaline soln., and this serves as a confirmatory test. The method, which is claimed to be of superior speed and accuracy to those already in use, is given in detail. J. W. D.

Hydrolysis of Polysaccharides by a Cation-exchange Resin and Identification of Monosaccharide Components by Paper Chromatography. R. E. Glegg and D. Eidinger. *Anal. Chem.*, **26**, 1365–1367 (Aug. 1954).

Studies in which Permutit Q (a polystyrenesulphonic acid type of cation-exchange resin) was used indicate that pentoses, methylpentoses, and aldohexoses are easily detectable by paper chromatography after heating with the resin for 48 hr., whereas ketoses are not. With di-, tri-, and poly-saccharides, the sugar spots are of max. intensity after 48 hr. in most cases, and the hydrolysis yields only those monosaccharides which are predictable on the basis of the known structural units. J. W. D.

Determination of Alkoxyl Groups. V—Selective Determination of Methoxyl Groups and Simultaneous Determination of Methoxyl and Ethoxyl Groups. G. Gran. *Svensk Papperstidning*, **57**, 702–708 (15 Oct. 1954).

Willstätter and Utzinger's trimethylamine method for the selective determination of methoxyl was improved by using *iso*propanol instead of ethyl alcohol as solvent for the trimethylamine. Tetramethylammonium iodide is so difficultly soluble in a 10% soln. of trimethylamine in *iso*propanol that no solubility correction is necessary. The precipitate forms very quickly, and can be filtered off immediately after distilling the sample with HI. The remaining alkoxyl groups can be determined in the filtrate. The absorption and filtration arrangements have been improved. The precision of the determinations amounts to about ± 2% with samples containing about 5 mg. of methoxyl and ethoxyl groups. S. V. S.

Determination of Phenolic Hydroxyl Content of Lignin Preparations by Ultraviolet Spectrophotometry. O. Goldschmid. *Anal. Chem.*, **26**, 1421–1423 (Sept. 1954).

The ultraviolet absorbance of an alkaline soln. of the sample is measured directly against that of a neutralised portion of the same sample. The phenol content of the sample is calc. from the absorptivity max. of the resulting difference curve, and the molar absorptivity max. of model phenols are similarly determined. The method is suitable for routine use; all details are given. J. W. D.

Ultraviolet Absorption Spectra as a Measure of Phenolic Hydroxyl Group Content in Polyphenolic Tanninlike Materials. L. F. Maranville and O. Goldschmid. *Anal. Chem.*, **26**, 1423–1427 (Sept. 1954).

The basis of the method is similar to that applied to the determination of the phenolic hydroxyl content of lignin (previous abstract). J. W. D.

Identification of Polymers. W. H. T. Davison, S. Slaney, and A. L. Wragg. *Chem. and Ind.*, 1356 (30 Oct. 1954).

The pyrolysates of polymers are subjected to gas-phase partition chromatography; the patterns of the peaks on the recorded chromatograms are sufficiently characteristic to permit identification of the polymers. The method is detailed, and eight chromatograms are reproduced. J. W. D.

Rheology of Solutions of High Polymers. VI—Absolute Rheological Determination of Molecular Weights of High Polymers. K. Edelmann. *Faserforsch. und Textiltech.*, **5**, 325–337 (Aug. 1954).

The viscosity η of a soln. of a high polymer is a function of the wt., form, and stiffness of a polymer mol. The absolute determination of the mol.wt. M from viscosity measurements requires a knowledge of viscosity–temp., viscosity–concn., and viscosity–flow gradient functions—

$$M = \frac{Kc_{\min}}{G_{\text{crit}}}$$

in which—

$$K = \frac{3RT}{\mu} \cdot \frac{\mathrm{d}(\ln \eta)}{\mathrm{d}(\ln T)}$$

($c_{\min}$ = concn. at which η/c is a min. (see J.S.D.C., **70**, 326 (July 1954)); G_{crit} = critical flow gradient (see J.S.D.C., **69**, 106 (1953)); μ = kinematic viscosity of solvent (strictly speaking, that of a soln. of concn. $c_{\min}$)). A. E. S.

Determination of the Osmotic Limit of Molecular Size. J. Corbière and R. Stuchlik. *Bull. Inst. Text. France*, (48), 61–75 (Aug. 1954).

An attempt to relate viscosimetric and osmotic measurements showed a constant relation between osmotic pressure and concentration valid for all polymers, solvents, and temperatures. A general method of linear extrapolation of molecular size is possible on the basis of a limited number of results. S. R. C.

PATENTS

Indicator Composition. E. F. Drew & Co. *USP* 2,663,692

A mixture of 50% of Ethyl Orange with suitable blue and red dyes provides an indication which not only gives a very sharp and clear end-point but also before the end-point is reached gives clear warning by a definite change in the colour. Thus an indicator operating within pH 3·8 and 4·0 consists of Ethyl Orange (2·0–2·5 g.), Alphazurine A (1·4–1·6 g.) and Fuchsin Red (0·4–0·6) in 1,000 c.c. of water. When added to an alkaline solution it gives a clear green. As titration proceeds it changes to grey at pH 4·2–4·3 and at pH 3·9–3·8 it changes sharply to bright purple. C. O. C.

Absorbency Measuring Device. Bleachers' Assocn. *BP* 717,315

A short capillary tube extends vertically downwards from a horizontally supported reservoir. The tube has an outlet in a true horizontal plane to enable a wetting liquor to be supplied from the reservoir through the tube to the material whose absorbency is to be measured. This material is held under uniform tension in contact with the tube and there are means to register electrically the time taken to wet a given area of the material. C. O. C.

X-Ray Scattering of Swollen Rayons (VI p. 62).

XV—MISCELLANEOUS

Thymolphthalein as Latent Colouring Agent for Vanaspati. A. B. Kalkarni and R. C. Shah. *J. Sci. Ind. Research* (India), **13B**, 382–383 (1954): *Chem. Abs.*, **48**, 11665 (10 Oct. 1954).

Incorporation of thymolphthalein (1 part) in vanaspati (10,000) readily shows up if the vanaspati is used for adulterating ghee or butter. It is unaffected by micro-organisms used for curdling milk. C. O. C.

PATENTS

Stabilising the Colour of Toilet Waters and Perfumes. Colgate-Palmolive-Peet Co. *USP* 2,664,383

Addition of 0·005–0·25% by wt. of benzoylresorcinol to perfumes, toilet waters, etc. containing dyes renders the colour fast to prolonged exposure to sunlight. C. O. C.

Colours for Margarine. Standard Brands. *USP* 2,652,334

Pellets made from an edible thixotropic aqueous gel in which is dispersed a fat-soluble water-insoluble dye can be embedded in margarine for prolonged periods without any diffusion of colour into the margarine and yet on kneading they readily liquefy at room temperature and mix with the margarine. C. O. C.

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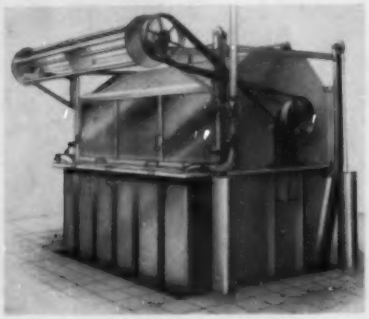
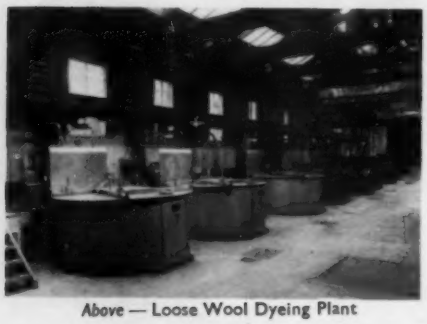
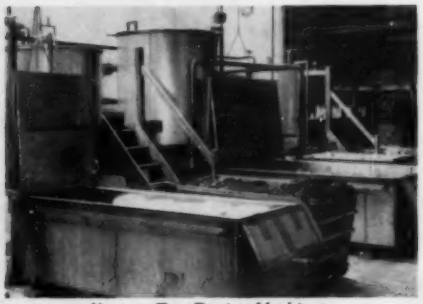


Above — Enclosed Piece Dyeing Machines



Above — Loose Wool Dyeing Plant



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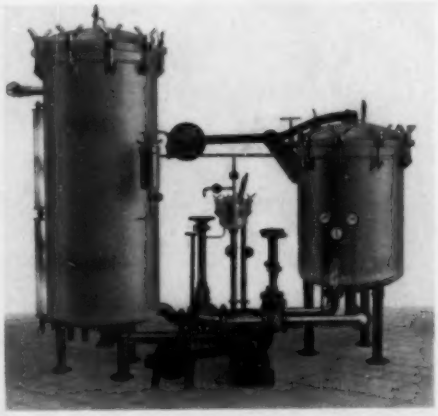

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Hubbard, C. S., c/o Cox Moore & Co. Ltd., Milnes Road, Long Eaton, Notts.

Kubba, S. M., 65 Haypark Avenue, Belfast, N. Ireland

Lascaris, L., 8 Queen's Road, Edgerton, Huddersfield, Yorks.

Mills, K. J., Shell Chemicals Ltd., Walter House, Bedford Street, Strand, London W.C.2

Priest, F., 10 St. Leonard's Road, Heaton Chapel, Stockport, Cheshire

Roulston, I. A. D., 22 Upper Malone Road, Belfast, N. Ireland

Warden, D. S., 32 Cemetery Road, Heckmondwike

The Society of Dyers and Colourists

ADVANCE ANNOUNCEMENT

NORTHERN IRELAND SYMPOSIUM

on

"Bleaching, Dyeing and Finishing Today"

will be held at

Portrush County Antrim Northern Ireland

from 13th to 17th September 1955

APPLICATIONS FOR ACCOMMODATION should be addressed in writing to the General Secretary, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* 25138-9)

SITUATIONS VACANT AND WANTED *etc*

Replies may be addressed "Box —, SOCIETY OF DYERS AND COLOURISTS," DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS.

SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

CITY OF BRADFORD CONDITIONING HOUSE

APPLICATIONS are invited from suitable candidates for the Superannuable post of SENIOR TEXTILE ANALYST for the physical and chemical testing of all types of textile materials from fibres to finished products. A sound and extensive practical experience is necessary, with ability to control technical staffs and to undertake work of an investigational character.

Preference will be given to candidates holding a University degree or the Associateship of the Textile Institute.

Salary will be in accordance with the A.P.T. Division, Grades III–IV (£600–£825 per annum) the commencing salary to be fixed according to qualifications and experience.

Applications accompanied by names of two referees and endorsed "Senior Textile Analyst" should reach me by 18th February 1955.

W. H. LEATHAM
Town Clerk

Town Hall Bradford 1

ASSISTANT TECHNICAL MANAGER, under 40, required by Textile Printers. Good knowledge of processing cottons and rayons required; technical qualifications and production experience both necessary; sound knowledge of colour application desirable. Required to take charge of Laboratory. Excellent prospects for right man. Commencing salary not less than £750 p.a. depending on suitability. Full details of qualifications, experience, etc. should be stated in applications, which will be treated in strict confidence. Box V60

AUSTRALIA. Dyer wanted to take charge of wool top and yarn dyehouse for old established firm near Sydney.

Write giving details of age, qualification, experience and salary level to Box V61.

CLOTH TESTING. Applications are invited from young men or women aged under 30 years, for the position of Cloth Tester to BERKERTEX, the Dress Manufacturers, in our factory at Plymouth, Devon, which is the most modern and the largest of its kind in the country. The job entails operating a small Cloth Testing Department for User Tests in wool, cotton, and rayon for colour fastness, strength, shrinkage, etc. Tests are made on sample lengths to assist in buying, and on bulk deliveries for check purposes. The West of England offers ideal living conditions, and housing can be arranged where necessary. Applicants for this important and interesting post should have technical qualifications and preferably some practical experience in cloth testing. Commencing salary would be commensurate with age, qualifications, and experience, full details of which should be sent to the Production Director, Berkertex, Crownhill, Plymouth.

COLOURIST required by Textile Printers. Must be fully qualified and have experience of Machine or Screen works— Furnishings or Dress. Age 25 – 40. Good salary and Prospects. Apply in confidence stating full particulars to Stead, McAlpin & Co. Ltd., Carlisle.

DYEHOUSE MANAGER. Old established firm of commission dyers and finishers situated twelve miles north of Derby, has a vacancy for a Dyehouse Manager to take charge of established modern plant for hank and pressure dyeing of webbings, tapes, and yarns in cotton, wool and latest synthetic fibres. Must be capable of using modern methods of control, both managerial and technical.

Applications for this pensionable staff appointment should include full details of age, training, experience and salary required, in strict confidence to The Managing Director, Stevensons (Dyers) Limited, Ambergate, Derbyshire.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, NOBEL DIVISION, requires for "Ardil" Factory, Dumfries, a Textile Chemist for Development and Technical Service work in dyeing and finishing of new fibres. Candidates, preferably with a University degree, must have a sound theoretical knowledge of dyeing and finishing. Several years practical experience of piece dyeing and finishing in the cellulosic field, including unions and synthetics, is essential. Salary according to age, qualifications and experience. Applications should be made in the first instance to the Staff Manager, 460 Sauchiehall Street, Glasgow C.2.

HEAD FINISHER— CHILE

LARGE AMERICAN ORGANISATION requires a MASTER FINISHER for its Textile Mills in Chile, South America. Applicants should have a wide experience in finishing and dyeing of cotton and rayon and also blends of cotton/rayon and rayon/wool. Should also have a thorough knowledge of crease resist and, if possible, Everglaze processes.

The appointment carries a substantial salary (partly paid in dollars) consistent with candidate's experience and qualifications. Home leave for employee and family with passages paid after three years. Unfurnished house with nominal rental will be provided.

Applicants please submit full details of age, preferably under 40 years, experience, technical qualifications, family status and salary required to Box W388, c/o Jackson's, 54 Old Broad Street, London E.C.2.

MIDLAND SILICONES LTD., an Associate Company of Albright & Wilson Ltd., require the following Technical Sales Staff in London and other centres.

(1) An Assistant to the Manager (Water Repellents Section) London.
(2) An Assistant to the Manager (Resins Section) London.
(3) A Technical Representative (London and South-East) based on London.
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Post 2— A science degree or qualification preferably in Paint Technology with experience in the surface coating industries and an interest in Silicone applications in these industries.

Posts 3 *and* 4— Science degree preferably in Chemistry or equivalent qualifications. Some experience in the Chemical or allied industries is desirable. Experience of sales representations or technical service in at least one of the following industries would be an asset: Rubber, Plastics, Textiles, Paper, Leather, Electrical Engineering, Paints and Resins.

All these posts are concerned with the marketing of a wide variety of Silicone Products and a high standard of technical competence together with an interest in Sales and Sales promotion is essential. Commencing salaries will be appropriate to age, qualifications and experience. The Company has a non-contributory pension scheme. Candidates, who should be aged 26 – 32, should write in the first instance for a detailed form of application, stating post desired, to the Staff Officer, Albright & Wilson Ltd., P.O. Box 3, Oldbury, Birmingham.

TEXTILE CHEMIST required for laboratory of bleach and dyeworks processing cotton and rayon piece goods. Must have technical and works' experience, aged under 30. Please reply, giving qualifications and experience to J. J. Hadfield Ltd., Garrison Bleach & Dyeworks, Birch Vale, near Stockport.

MISCELLANEOUS

THE Society has several requests for back numbers of the *Journal* but the following issues are out of stock. If any member wishes to dispose of any of these copies, the Society will re-purchase them at 2*s.* per copy. January 1939 to December 1944; February to March 1945; January to March, and June 1946; January to June 1952; January and July 1954. Replies to be addressed to the General Secretary, Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford.

WANTED. Proceedings of a symposium on Fibrous Proteins held at The University, Leeds, on 23rd, 24th and 25th May 1946. Replies to be addressed to the General Secretary, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford.

ADDRESSES WANTED

Bryne, L. F., formerly c/o Wm. Walker & Sons Ltd., Research Dept., Rose Hill Tannery, Bolton, Lancs.

Meier, P. W., formerly of Oberwilerstrasse 38, Basle, Switzerland

Nixon, I. G., formerly of Adriaan Goekooplaan, 105 Flat Gebouw Catsheuvel, The Hague, Holland

Salomon-de-Freidberg, J. A., formerly of 11a Wiverton Road, Sherwood Rise, Nottingham

Young, L. A., formerly of 51 St. Michael's Lane, Headingley, Leeds 6

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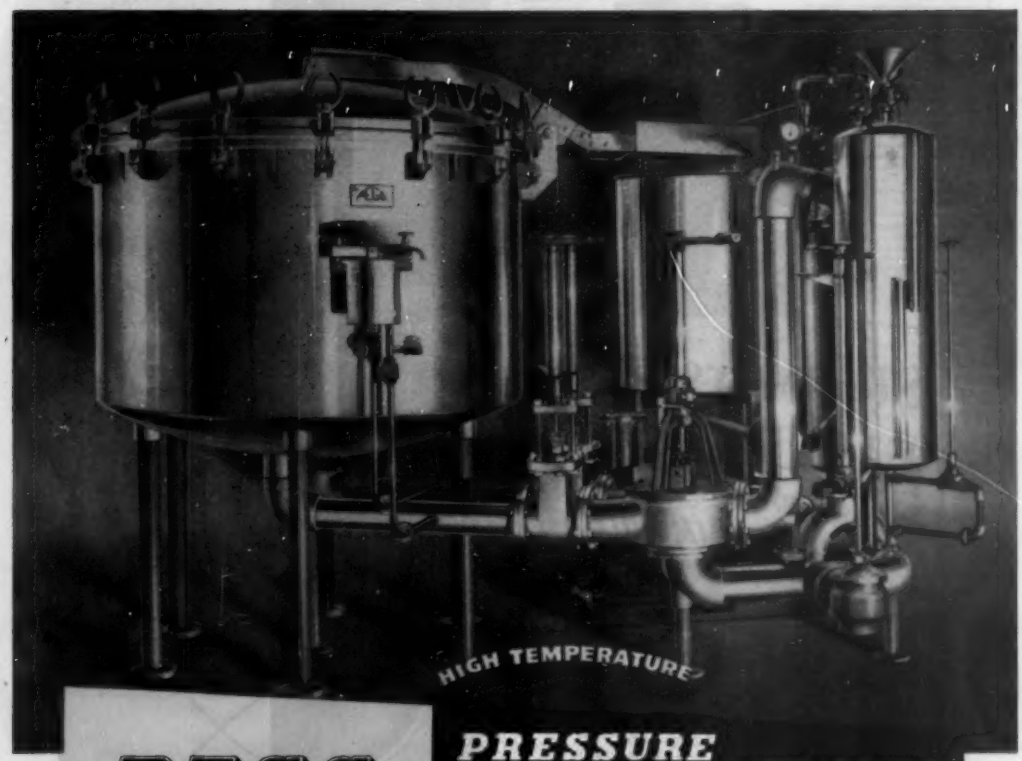

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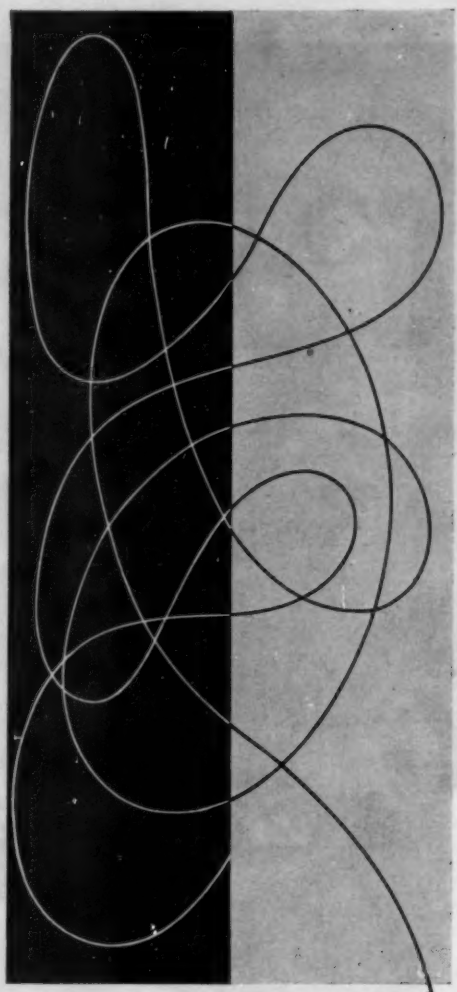

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The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given below.

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Reprints of all lectures and communications are available after publication to members and non-members of the Society. The charges (postage included) are as follows— Single copies 2s. 6d. each; per dozen copies up to and including 8 pages, 12s. 6d., and for papers occupying more than 8 pages of the *Journal*, 17s. Orders should be addressed to "The Society of Dyers and Colourists, 19 Piccadilly, Bradford 1". They can be accepted only if accompanied by remittance and if received immediately after publication of the paper.

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